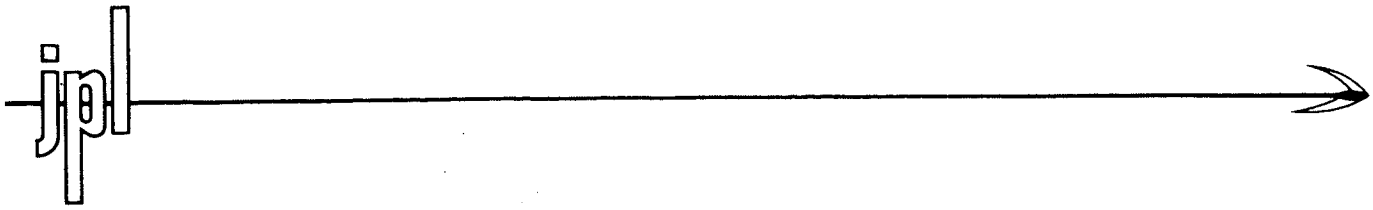

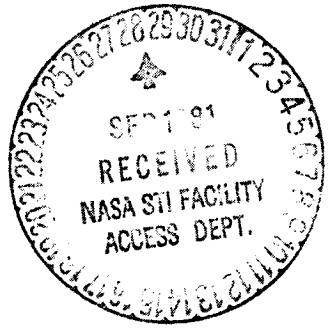

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JET PROPULSION LABORATORY

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

LETTER REPORT

FORENSIC SCIENCES MICROANALYSIS SEMINAR

TASK 143

March 1970 through May 1970

650-116

June 15, 1970

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LETTER REPORT

FORENSIC SCIENCES MICROANALYSIS SEMINAR
TASK 143

I. INTRODUCTION

In the summer of 1968, the Special Programs Office of the National Aeronautics and Space Administration expressed an interest in possible ways in which NASA's technical competence could be of assistance in public safety support activities.

A JPL study conducted during the closing months of 1968 culminated in the establishment of the NASA/JPL Space Technology Applications Office Public Safety Support Activities group. This study identified a number of scientific instruments and analytical methodologies used in the development and implementation of space exploration, which should be directly applicable to the needs of forensic scientists in processing physical evidence materials.

During 1969, the needs of the law enforcement community were further assessed in the context of space instrumentation. The annual meeting of the American Academy of Forensic Sciences in February indicated an acute need for training in microanalytical techniques and for familiarization with the instruments and methods developed during the past few years.

In June, a poll of the California Association of Criminalists verified this need and confirmed an interest in obtaining such training and familiarization.

As the initial step in a training program, a seminar was planned to provide a comprehensive overview of analytical equipment and technology used in the space program. It was decided to limit the audience by inviting only members of the California Association of Criminalists, but, in order to encourage participation by a representative cross section of the group, to hold the sessions on weekends and to attempt to obtain a state grant to defray travel and living expenses of the participants.

Accordingly, a task plan was prepared, submitted to Headquarters, and approved by Headquarters in February 1970. Subsequent schedule conflicts were resolved by combining the two weekend sessions originally planned into one three-day meeting to be held Friday, Saturday, and Sunday, May 15-17, 1970.

This report summarizes the activities and results of STA Task 143, carried out in March, April, and May of 1970.

II. OBJECTIVES AND CONSTRAINTS

As stated in the task plan, the primary objective of this task was to provide forensic scientists with a knowledge of the potential value of advanced microanalysis instruments and techniques used in the space program. The secondary objective was to give JPL/STA additional insight into the needs and problems of forensic scientists as the basis for further transfer of space technology to the area of public safety.

Because this task represented a start by JPL/STA in the area of transfer of broad segments of technology, it was desirable to test user reaction with a small audience, whose interest was indicated by membership in the California Associatian of Criminalists or by the recommendation of directors of county or state laboratories.

While the speakers had some prior exposure to the fundamentals of forensic sciences, they were not asked to investigate the specific needs and requirements of the field. The majority of the presentations were planned as straight-forward descriptions of equipment and techniques used in day-to-day work in the space program. Since several of the speakers have been involved in current STA activities in the field of public safety, discussions of such efforts as automated drug identification, fingerprint image enhancement, and soils characterization by thermoluminescence were incorporated into the presentation material.

The speakers were assisted in selecting suitable material to include in their presentations by Lowell Bradford, Director of the Santa Clara County Laboratory of Criminalistics and consultant to the STA office.

III. THE SEMINAR

As a result of 80 invitations mailed on 24 April 1970 to 80 forensic-scientist members of the California Association of Criminalists and to directors of laboratories in California, some 75 reservations were made. Out of the 75 reservations a total of 56 attended the seminar.

The seminar consisted of eight presentations, ranging in length from one and one-half to three and one-half hours. Dr. Robert Landel, Manager of the Polymer Research Section at JPL, chaired the seminar, and, with the assistance of Lowell Bradford, set the stage for the meeting with a brief keynote address pointing out the areas in which space sciences may be of value to forensic sciences. Topics, speakers, and a capsule description of each presentation are as follows:

X-RAY DIFFRACTION, X-RAY FLUORESCENCE, AND THE ELECTRON MICROPROBE

A. A. Chodos

Mr. Chodos discussed the camera and the spectrometer techniques of x-ray diffraction and x-ray fluorescence as analytical tools, and the use of the electron probe for qualitative analysis. Physical and operating characteristics, sensitivity, cost and applications of the three methods were described.

NUCLEAR MAGNETIC RESONANCE

S. L. Manatt

After presenting the general theory and the physical, functional, and operational characteristics of NMR, Dr. Manatt explained the basic NMR effect, the chemical applications of nuclear magnetism, and the NMR of barbiturates. JPL usage of NMR and its potential applications to criminalistics were discussed.

THERMOANALYTICAL METHODS

R. A. Rhein

Dr. Rhein discussed the various thermal techniques (DTA, TGA, TMA, ETA, effluent gas detection and analysis, and thermoluminescence), and their use in identifying and characterizing organic and inorganic materials, with particular application to criminalistics.

CHROMATOGRAPHY AND MASS SPECTROMETRY

H. G. Boettger

An exposition of the work being done in gas chromatography and mass spectrometry for planetary purposes and its application to criminalistics was discussed. Recent developments in pyrolysis and thin layer chromatography were included.

ADVANCES IN ULTRAVIOLET AND INFRARED SPECTROMETRY

D. D. Lawson

Mr. Lawson presented a paper on the nature of UV and IR spectra, the specific spectra of each, their instrumentation, and their applications.

SCANNING ELECTRON MICROSCOPE APPLICATION POTENTIAL IN CRIMINALISTICS

J. R. Devaney

Mr. Devaney discussed the various modes of the scanning electron microscope: emissive, reflective, absorptive, conductive, and luminescent. S.E.M. applications to physical evidence materials were described and illustrated.

COMPUTER APPLICATIONS

C. S. Christensen

Dr. Christensen explained what a computer is, some of the things it can do, some of the things it cannot do, and some of the ways it can be of help to the criminalist.

IMAGE PROCESSING AND ENHANCEMENT

R. J. Blackwell

Mr. Blackwell presented the preliminary results of a study on the application of image enhancement by computer methods to fingerprints. He discussed the scanning system, the four image processing goals, and the use of maxima/minima detection in fingerprint enhancement.

A copy of the agenda and expanded outlines/abstracts of the eight presentations with selected portions of the visual aids used are included as Appendix A.

During the seminar, it was decided to include a brief progress report on AUDRI (STA Task 132, Automated Drug Identification, which is just completing phase 0), and to include it on the demonstration tour. (This addition is not indicated in Appendix A.)

An informal workshop session was held Saturday evening, May 16, to discuss the effectiveness of laboratory operations and the applicability to the forensic sciences of such systems engineering tools as operations research and effectiveness modeling. Fifty-two forensic scientists and twelve JPL representatives participated.

The seminar was concluded with laboratory demonstrations at JPL and Caltech of the various instruments actually analyzing forensic evidence materials. Forty-three criminalists attended these demonstrations.

All presentations and question and answer sessions were video taped, with the expectation that the tapes may serve as an inexpensive means of presenting the material to a much wider audience.

Proceedings were also audio taped, have been transcribed, and are currently being edited. A final version will be published complete with all visual aids and commentary and will be provided to each seminar registrant by 3 August 1970.

IV. RESULTS

On the final day, attendants were requested to assess the effectiveness of the seminar as a means of technology transfer, and to rate the value of each technique discussed in the context of applicability to their particular forensic problems.

The consensus of opinion was that the idea of exposing a large number of criminalists to the new methods and techniques of space sciences was excellent and the exchange of information should be continued. The attendants felt that the seminar was well-planned and executed, and some indicated that it should be repeated after they have had time to gain a better understanding of specifics. It was further suggested that other persons involved in criminal justice, such as police administrators, attorneys, and judges, be invited to attend semi-technical meetings to acquaint them with new technologies.

The continued presence of the speakers over the three-day period and their availability for informal discussion was considered particularly valuable in enhancing the information exchange.

Many of the criminalists stated that if it could be arranged for them to work with JPL experts in the equipment areas, the effectiveness of the seminar would be increased. They also wanted to know specifically who at JPL would be available for consulting, without involvement in actual analytical work, on unusual cases or technical problems. It was also proposed that the talents of JPL people might be of help in systems analysis.

The general opinion was summed up by one attendant who wrote, "People who attended the seminar should be kept informed on what happens next. This relationship should at all costs be kept alive."

The following tabulation of the presentations was compiled from individual evaluation sheets completed by the attendants at the close of the seminar:

Presentation	Very significant	Average significance	Not significant
Advances in Ultraviolet and Infrared Spectroscopy	34	7	1
Scanning Electron Microscopy Application Potential in Criminalistics	31	8	1
A Review of the Current Status of Mass Spectrometry, Chromatography, and Pyrolysis as Tools for the Detection and Identification of Complex Organic Compounds	30	11	1
Fingerprint Image Enhancement by Computer Methods	30	9	1
X-Ray Diffraction, X-Ray Fluorescence, and the Electron Microprobe	25	10	0
Thermoanalytical Methods	25	9	0
Computer Applications	22	18	2
Informal Workshop — Effectiveness of Laboratory Operations	21	15	4
Nuclear Magnetic Resonance	13	15	7

In analyzing these ratings, it should be noted that the scientific educational background of the attendants ranged from a few people with no degrees to one with a PhD in Criminology. Most of the criminalists have a basic knowledge of UV and IR spectrometry. As might be expected, they rated "Advances in Ultraviolet and Infrared Spectrometry" the most significant, because it gave them new techniques in the use of their instruments which they could immediately apply to their problems without any sizeable expenditures of time or money.

However, also because of their familiarity with the technique, they stated that the presentation should have had more emphasis on advances and less on basic fundamentals.

The advantages of "The Scanning Electron Microscope — Application Potential in Criminalistics" were immediately apparent to men versed in the use of optical scopes. They expressed interest in developing a liaison with Mr. Devaney and felt that there should be more research in applications of the S. E. M. to criminalistics.

"A Review of the Current Status of Mass Spectrometry, Chromotography, and Pyrolysis as Tools for the Detection and Identification of Complex Organic Compounds" was judged to be one of the most valuable outputs of the seminar. Those participants who have a gas chromatograph intended to immediately apply some of their new knowledge to their present problems. The criminalists believed that the mass spectrometer would be useful for rapid drug identification from such evidence as body fluids. Because of the time constraint, thin layer and micro dry column chromatography were not as fully discussed as the MS and GC. Consequently, there were several suggestions that TLC and MDC be covered at a future date as separate topics.

"Fingerprint Image Enhancement by Computer Methods" produced several comments from the audience about cases that probably could have been solved if this method of enhancement had been available. They agreed that this is an area in which they all have problems, and they would like to examine the technique further with a criminalist participating in the experiments.

Although the techniques of "X-Ray Diffraction, X-Ray Fluorescence, and the Electron Microprobe" were new to most of the group, its many applications to problems not now being solved were apparent. The microprobe was rated as probably the most significant of the 3 techniques. A few felt there was more technical detail given than was needed.

"Thermoanalytical Methods," were assessed by many as probably having the most rapid application of any of the techniques presented, with the exception of UV, IR, and GC, which most of them have. The participants felt that thermoanalysis may become a very important tool, but that they need more information on the uniqueness of characterizations for legal presentation.

The consensus of opinion on "Computer Applications" was that it is a field with great potential use and offers hope for the future in handling the increasing volume of work. It was also generally agreed that this is recognized as an area of neglect in criminalistics, but that forensic scientists need physical access to computers, support to implement programs, and more understanding of the subject before practical applications can be developed and used in forensic science.

"Effectiveness of Laboratory Operations," the subject of the informal workshop, was described as a topic covered before in C.A.C. meetings with little outcome. However, 21 people felt it was a very significant topic at this seminar. Therefore it should probably be developed further.

"Nuclear Magnetic Resonance" was considered potentially valuable for structural ID and for its applicability to areas necessary for a data base to qualify methods for court presentation.

One frequent comment, both written and oral, expressed concern over the cost of much of the equipment, in particular, the microprobe, the S.E.M., the mass spectrometer, and computers. Such comments as, "Very valuable, but too expensive for the typical crime lab; very good, if we could afford to have one" seem to imply resignation to the idea that these new instruments are out of reach. This attitude prevailed in spite of the fact that the group had just listened to Mr. Douglas Roudabush, Executive Officer of the California Crime Technical Research Foundation at Sacramento, California, tell them where the money is available and how to "relate problems to action to money." The CCCJ is faced with the problem of reorienting the forensic scientist to his monetary environment so that he can "relate problems to action to money."

V. FOLLOW-UP PLANNED AND RECOMMENDED

As previously noted, the transcript of the proceedings is being edited and will be distributed to all participants in about six weeks. At that time attendees will be requested to reiterate their assessment of the seminar. It is further planned to use a more detailed questionnaire in November or December to determine whether the attendees have made any use of the seminar and published proceedings, and whether it has stimulated any new efforts in experimental work or additional search for information.

We plan also to request suggestions about whether the material presented should be further refined, or the emphasis changed; and as to whether this type of technology transfer should be continued and, if so, at what pace and to what depth.

A low-key start has been made in offering to provide forensic scientists with technical assistance in attacking specific problems which may arise in the immediate future. Definitive interest has already been expressed in image enhancement, scanning electron microscopy, and thermoluminescence. The director of the Orange County crime laboratory has spent two days at JPL experimenting with the TOL as a means of rapid categorization of forensic evidence materials.

Consideration is being given to editing the video tapes of the proceedings, probably including some footage of the subject equipment in operation, to form the nucleus of a library of two to four hour presentations of analytical instrumentation capable of widespread inexpensive dissemination.

Plans are also under consideration to repeat the seminar for midwestern and eastern audiences at some future date. No serious attempt has been made to work out the logistics as yet, and the content of any future seminar will obviously be affected by the results of the above mentioned detailed questionnaire to be sent to the attendees.

APPENDIX A

Agenda and Abstracts

(Reprint of material distributed at the seminar)

Forensic Sciences Microanalysis Seminar

THE POTENTIAL VALUE OF ADVANCED INSTRUMENTATION TECHNOLOGY FOR THE FORENSIC SCIENTIST

JPL-STA 650-111 23 June 1970

Presented by

The Space Technology Applications Office
The Jet Propulsion Laboratory, California Institute of Technology

May 15, 16, and 17, 1970

Under the Sponsorship of

The National Aeronautics and Space Administration

and

The California Council on Criminal Justice

To Be Held At

Von Karman Auditorium, Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California

AGENDA

Chairman: Dr. Robert F. Landel
Manager, Polymer Research Section
Propulsion Division
Jet Propulsion Laboratory

FRIDAY, May 15, 1970

8:30 - 9:30AM	Registration	
9:15 - 9:30AM	Coffee & Donuts	
9:30 - 9:35AM	Welcome	Dr. William H. Pickering Director Jet Propulsion Laboratory
9:35 - 10:15AM	Keynote: "A Brief Survey of Space Instrumentation-What the Space Sciences can offer the Forensic Sciences"	Dr. Robert F. Landel Manager, Polymer Research Section Propulsion Division Jet Propulsion Laboratory and Mr. Lowell W. Bradford Director, Laboratory of Criminalistics Office of the District Attorney County of Santa Clara
10:30 - 12:30PM	Presentation: "X-Ray Diffraction, X-Ray Fluorescence, and The Electron Microprobe"	Mr. Arthur A. Chodos Senior Spectroscopist Div. of Geological Sciences Calif. Institute of Technology
12:30 - 1:30PM	Luncheon (JPL Cafeteria)	
1:30 - 3:00PM	Presentation: "Nuclear Magnetic Resonance"	Dr. Stanley Manatt Member, Technical Staff Physics Section Space Sciences Division Jet Propulsion Laboratory
3:00 - 3:10PM	Break	
3:10 - 5:00PM	Presentation: "Thermoanalytical Methods"	Dr. Robert A. Rhein Senior Scientist Polymer Research Section Propulsion Division Jet Propulsion Laboratory

Agenda

FRIDAY, May 15, 1970(Contd)

5:30 - 6:30PM	Demonstration: "X-Ray and Microprobe Equipment" (Mudd Hall, Cal Tech)	Mr. Arthur A. Chodos Senior Spectroscopist Div. of Geological Sciences Calif. Institute of Technology
6:30 - 7:30PM	Social Hour (Athenaeum - Cal Tech)	
7:30 -	Dinner (Athenaeum - Cal Tech)	

SATURDAY, May 16, 1970

8:30 - 12:00AM	Presentation: "A Review of the Current Status of Mass Spectrometry. Chromatography, and Pyrolysis as Tools for the Detection and Identification of Complex Organic Compounds"	Mr. Heinz G. Boettger Senior Scientist Bioscience Section Space Sciences Division Jet Propulsion Laboratory
10:00 - 10:10AM	Break	
12:00 - 12:30PM	Tour of Space Flight Opeations Facility	
12:30 - 1:30PM	Luncheon (JPL Cafeteria)	
1:30 - 3:30PM	Presentation: "Advances in Ultraviolet and Infrared Spectrometry"	Mr. D. David Lawson Senior Scientist Polymer Research Section Propulsion Division Jet Propulsion Laboratory
3:30 - 3:40PM	Break	
3:40 - 5:10PM	Presentation: "The Scanning Electron Microscope - Application Potential in Criminalistics"	Mr. John R. Devaney Senior Engineer Electronic Parts Eng. Section Engineering Mechanics Div. Jet Propulsion Laboratory
6:00 - PM	Dinner (Athenaeum - Cal Tech)	

Agenda

SATURDAY, May 16, 1970(Contd)

7:30 - PM	Informal Workshop: "Effectiveness of Laboratory Operations" (Athenaeum - Cal Tech)	Moderator: Mr. Robert G. Chamberlain Member Technical Staff Systems Analysis Section Mission Analysis Division Jet Propulsion Laboratory

SUNDAY, May 17, 1970

9:00 - 10:20AM	Presentation: "Computer Applications	Dr. Carl S. Christensen Member, Technical Staff Operations & Programming Staff Data Systems Division Jet Propulsion Laboratory
10:20 - 10:30AM	Break	
10:30 - 12:00AM	Presentation: "Fingerprint Image Enhancement by Computer Methods"	Mr. Richard J. Blackwell Sr. Applications Engineer Image Processing Appls.Group Science Data Analysis Section Space Sciences Division Jet Propulsion Laboratory
12:00 - 12:20PM	Summary and Conclusions	Mr. Lowell Bradford Director, Laboratory of Criminalistics Office of the District Attorney County of Santa Clara
12:20 - 1:20PM	Luncheon (JPL Cafeteria)	
1:20 - 4:30PM	Instrument Demonstrations	

The majority of the instruments will be shown analyzing actual forensic evidence material.

Scanning Electron Microscope	158-106D
Image Processing Laboratory	168-435
NMR	183-818
GC/MS	183-810
TGA, TOL, UV, IR, etc.	183-328

4:30 PM Buses depart for airports

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FOREWORD

This document contains selected portions of the material presented at the Forensic Sciences Microanalysis Seminar. A report of the entire proceedings, including all speeches and illustrations, will be sent as soon as possible to each person attending the Seminar.

X-RAY DIFFRACTION, X-RAY FLUORESCENCE, AND THE ELECTRON MICROPROBE

A. A. Chodos

California Institute of Technology
Pasadena, California

I. INTRODUCTION

X-ray diffraction was discovered by Laue in 1912. Within two years the Braggs had simplified Laue's equations into the Bragg law ($n\lambda = 2\,d \sin\theta$) and had determined the crystal structure of copper. The technique can be used to identify or determine the structure of any crystalline material as no two compounds will give the exact same diffraction pattern.

X-ray fluorescence dates to Barkla's work in 1911 which demonstrated that an element emitted characteristic radiation when stimulated by X-radiation of a slightly shorter wavelength (greater energy). Moseley established in 1913 that the frequency of the characteristic lines is proportional to the square of the atomic number. By 1920, Hevesy was using the characteristic X-rays for chemical analysis, and in 1923 Coster and Hevesy proved the existence of Hf by its X-ray spectrum. Hevesy wrote the book on chemical analysis with X-rays in 1932, and the only real changes since then have been in the sophistication of the instrumentation and speed of analysis. What took Hevesy a day can now be done in 10 sec.

The concept of using a focused beam of electrons to generate characteristic X-rays from a small area on the surface of a sample came from electron microscopy, and Hillier (RCA) took out a patent in 1943. Hillier never built an instrument, and the first true microprobe was built by Castaing & Guinier at

the University of Paris. Castaing's thesis in 1951 represents the definitive work in the field. The first commercial instrument was produced around 1960, and there are now some 800 in use in the world.

Modern instrumentation for these techniques are shown in Figs. 1-1 and 1-2.

II. CHARACTERISTICS

A. PHYSICAL AND FUNCTIONAL

1. Repeatability:

   Repeatability of all three techniques is excellent.

2. Quantitation:

   In quantitative analysis using the electron microprobe the best work yields results which are equal to or better than any other analytical technique for major elements. For example, major element mineral analyses which would require 0.5 - 1 g of sample for chemical analysis can be performed on individual grains (yielding variations within and between grains rather than a composite analysis) with summations between 99 and 101% at a rate of about 15 sec per point for three elements or about 1500-2000 points analyzed for three elements per day. This amount of data cannot be handled without a computer. In addition, for quantitative work, it is necessary to calculate the interactions between the elements making up the sample, and this is only practical with computer processing.

3. Sensitivity:

   a. <u>X-ray Diffraction:</u>

      Sensitivity and accuracy are a function of how much time and effort is put into the analysis and how sophisticated the equipment is. A rule of thumb is that in routine X-ray diffraction the limit of detection will be about 5 weight percent. Highly crystalline materials with strong diffraction peaks will often be detectable to under 1%. Special techniques are available to increase the sensitivity at the cost of greatly increased time of analysis. The best quantitative work reported usually indicates a precision of ± 2 weight percent. Sensitivity and accuracy come at a price. For example the difference between ± 5% and ± 2% might represent an order of magnitude difference in effort.

b. X-ray Fluorescence Spectroscopy:

As each element has its own characteristic spectrum, or "fingerprint", and the X-ray spectra have few lines for each element, possibilities of overlap or confusion are few. Current standard instrumentation enables elements above sodium (atomic number 11) in the periodic table to be determined. Sensitivities for the elements below atomic number 15 would not be as good as for the other elements. Depending upon the instrumentation available and the sample matrix, sensitivities of 100 ppm would be possible for most elements. However, an extreme case, such as vanadium in oil, can have a sensitivity of 0.01 ppm (see Fig. 1-3).

c. Electron Microprobe:

The microprobe is essentially an X-ray tube in which the sample is the target for the electron beam. Since electron beam diameters of 0.02 - 0.05 microns can now be obtained routinely, analyses can be obtained from extremely small volumes of samples and microgram quantities can be determined. Elements from beryllium (atomic number 4) can now be detected, with best results above atomic number 10. Depending on the sample matrix, detection limits of 100 ppm are not usual. Figure 1-4 shows a histogram of summations of 166 analyses performed by graduate students. The variations would be less if all were analysed by an experienced operator. Figure 1-5 shows a qualitative analysis by microprobe of a small crater in a specimen of felspar brought back from the moon by Apollo 11.

4. Sample Preparation:

X-ray diffraction and the other techniques discussed in this presentation are generally referred to as "non-destructive" in that the sample put into the instrument is not destroyed. However, this should not be confused with the fact that the original sample must often be altered in some way to put it into a form suitable for analysis. The sample may come back in a form where it can be reanalyzed but will be otherwise worthless. Sample sizes differ for the two principal techniques used in X-ray diffraction. The camera technique is used primarily for small samples with a fraction of a milligram supplying sufficient material for identification purposes. The spectrometer technique is used primarily for larger samples (from about 100 mg up) and for quantitative analysis.

Most X-ray fluorescence spectrographs require sample sizes in the gram range. However, since the analysis is of a shallow surface layer, the sample may be spread out. The requirement is that the minimum thickness of a few hundreths of an inch be exceeded. Samples may be solid or liquid. Again, it should be noted that although the sample is not destroyed during the analysis, it may have to be cut to a specific size or powdered or dissolved in order to perform the particular analysis required.

Although little sample preparation is necessary for qualitative analysis with the electron microprobe, the sample must be electrically conducting. A non-conducting sample such as a rock can be coated with a thin film of carbon, aluminum or other conductor. For quantitative analysis, it is important that the sample be flat on a micron scale to prevent absorption effects due to shadowing. This usually involves mounting and polishing the sample.

B. OPERATIONAL

1. Time for Analyses:

The X-ray diffraction camera techniques are slow, since exposures run 10-20 hr. The spectrometer is much faster with a complete record obtainable in approximately 1 hr. Specific determinations often take only a few minutes.

As an analytical tool, X-ray fluorescence has proven to be considerably faster than chemical analysis and at least as accurate. This is primarily because there are no cumulative errors in X-ray fluorescence analysis. Each measurement is independent and a function of counting statistics. A single determination will often take only 60 sec. As in other spectrographic techniques, X-ray fluorescence is dependent upon known standards, and this often leads to dependence on chemical analyses.

The analysis time of the electron microprobe is a function of how demanding you choose to be in terms of precision and accuracy and the degree of automation available on the instrument. A complete qualitative element scan which would take 45 min of machine time on a normal three-channel instrument would take 4 to 6 min on an automated instrument.

C. COSTS

X-ray diffraction instrumentation costs from under $10,000 to over $70,000, while the equipment for X-ray fluorescence spectroscopy ranges in price from about $20,000 to approximately $80,000. Microprobes are available starting around $60,000; however, most instruments cost $100,000 and up.

III. APPLICATIONS

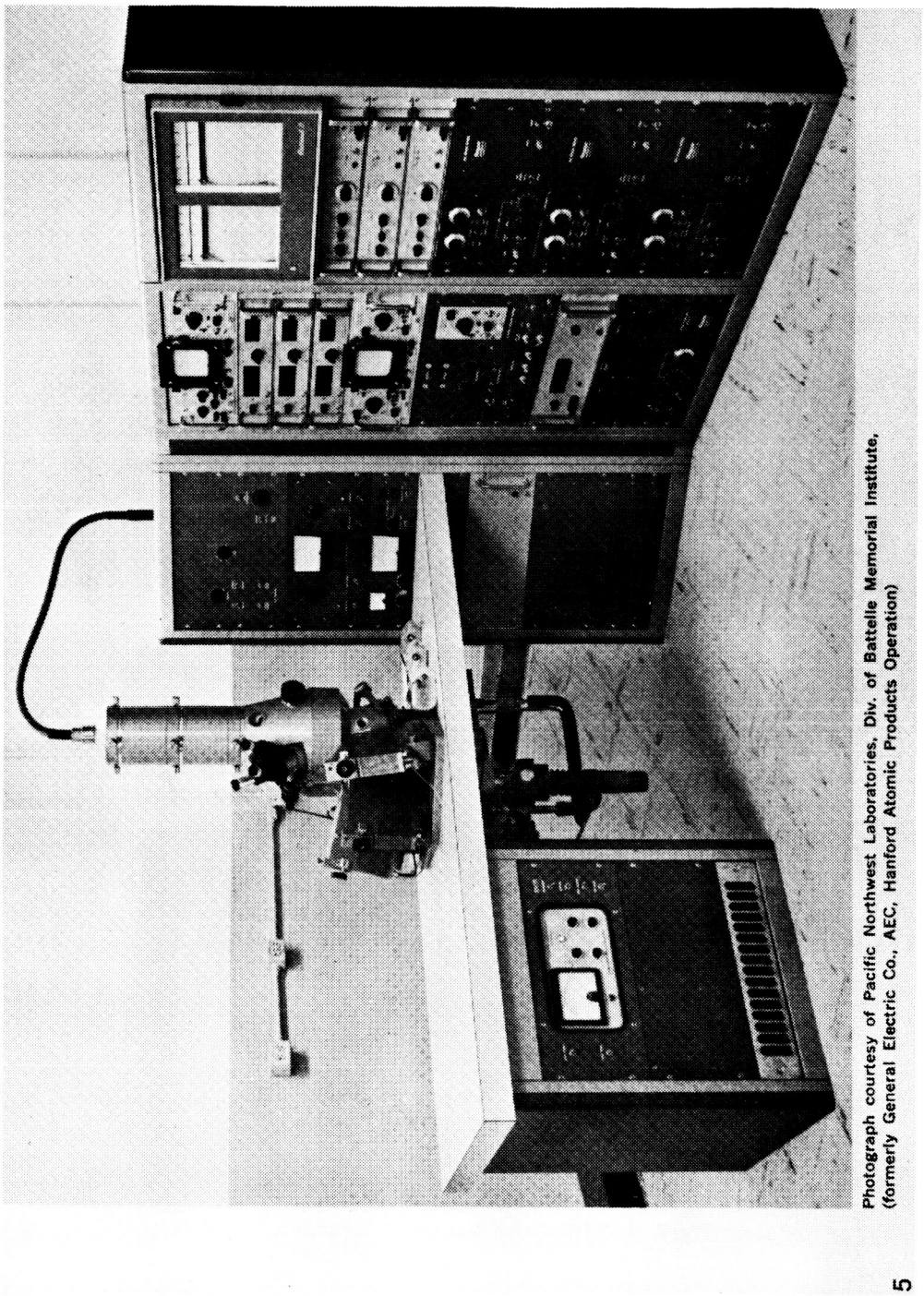
In this section, techniques used to analyze and identify a wide variety of samples are explained and illustrated. The applications of these techniques, with particular emphasis on their usefulness to the criminalist, are discussed.

IV. SUMMARY AND CONCLUSIONS

X-ray diffraction, X-ray fluorescence spectroscopy, and the electron microprobe are three modern techniques of great sensitivity and value in the analysis and identification of a broad spectrum of materials. These techniques can be successfully applied to many of the problems encountered in the criminalistic laboratory.

Fig. 1-1. Top: Diffractometer, Small Powder Camera, Large Powder Camera

Bottom: X-ray Fluorescence Spectrometer



Photograph courtesy of Pacific Northwest Laboratories, Div. of Battelle Memorial Institute, (formerly General Electric Co., AEC, Hanford Atomic Products Operation)

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Fig. 1-2. Electron Microprobe

ELEMENT	MATERIAL ANALYZED	MINIMUM DETECTED
SULFUR	FUEL OILS	0.02 wt. %
LEAD	GASOLINE	0.1 ml TETRAETHYL/gal
MANGANESE	GASOLINE	0.1 gm/gal
BARIUM	LUBRICATING OILS	0.1 wt %
VANADIUM	POWDERED CATALYST OIL COKE	0.01 wt % 0.01 ppm 0.001 wt %
PLATINUM	POWDERED CATALYST	0.6 wt %
BROMINE	INSECTICIDES	0.02 wt %

Fig. 1-3. Industrial Applications of X-ray Fluorescence

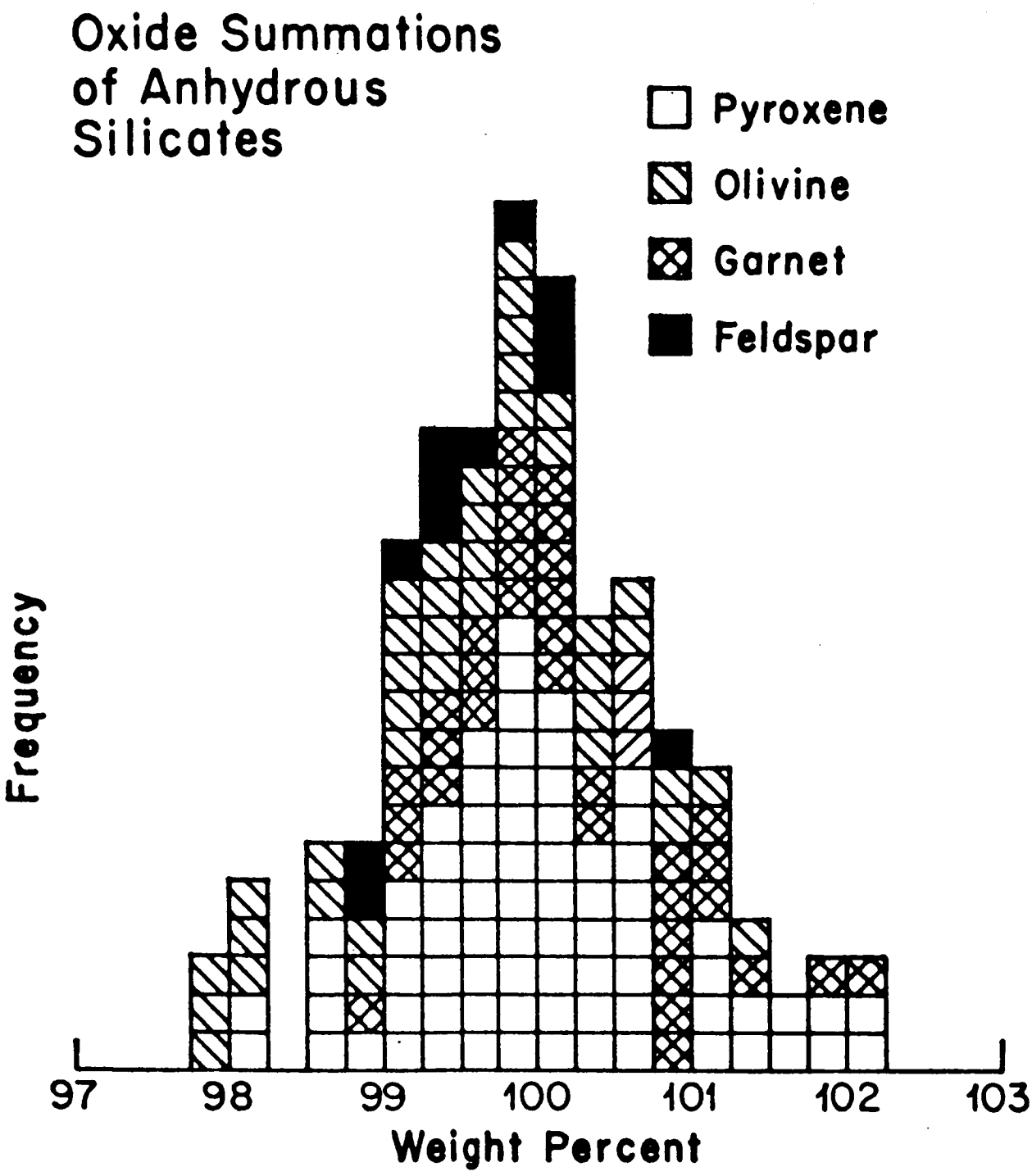
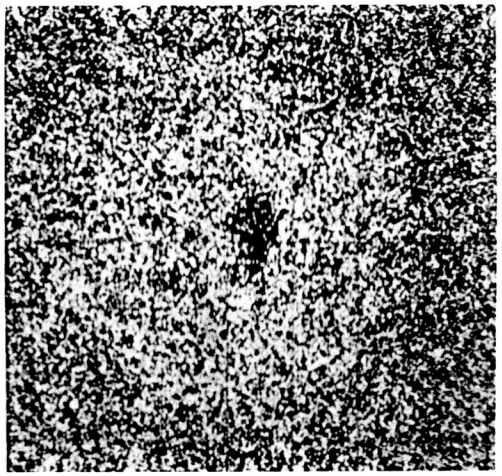


Fig. 1-4. Histogram of Oxide Summations of Anhydrous Silicates.



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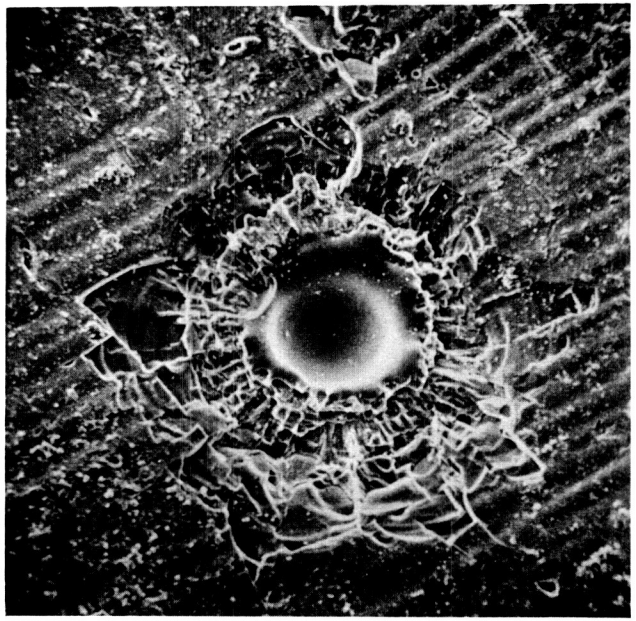

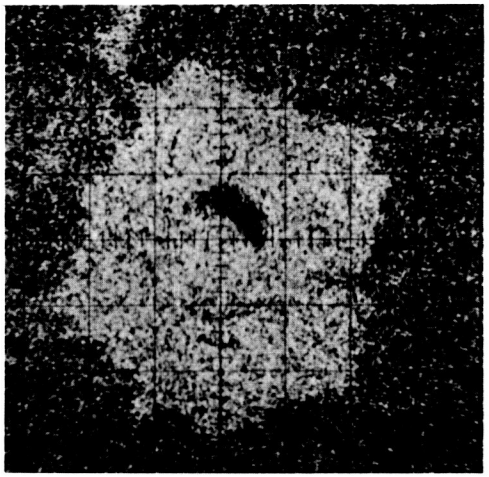

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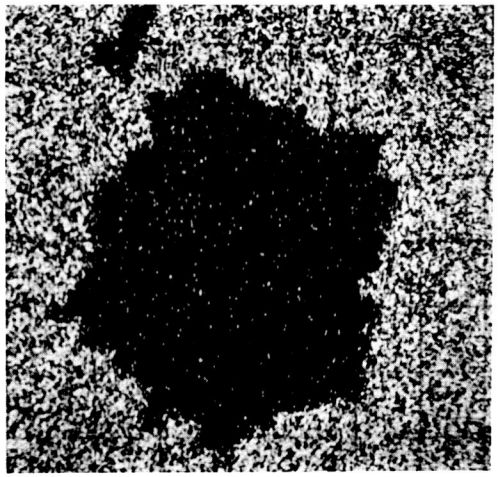

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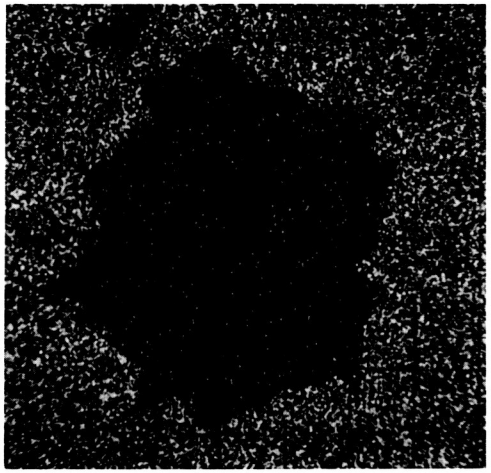

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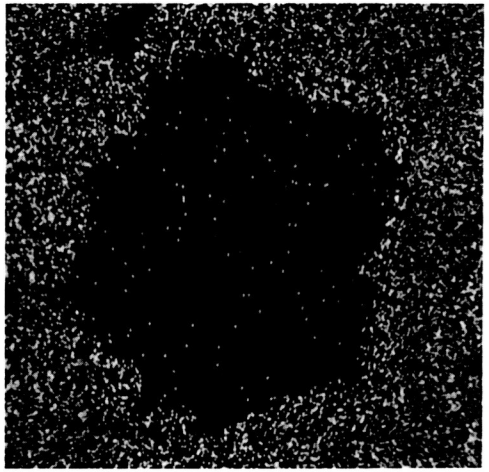

Ti

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Figure 1-5. Zap Crater on Surface of Felspar Crystal Picked from Lunar Soil.

175 MICRON FIELD

NUCLEAR MAGNETIC RESONANCE

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Jet Propulsion Laboratory, California Institute of Technology
Pasadena, California

I. INTRODUCTION

A. GENERAL THEORY

Nuclear magnetic resonance (NMR) spectroscopy is one of the newest and most spectacular techniques available to chemists for the elucidation of molecular structure and chemical analyses of organic molecules. The NMR effect arises because a large number of types of atomic nuclei possess spin angular momentum besides charge and mass. When a sample of matter containing magnetic nuclei is subjected to an RF field in the 4 to 220 MHz range, along with a strong magnetic field, it is possible to cause changes of the magnetic nuclei from one magnetic state to another. These changes can be detected readily through their effects on electronic circuits. The system for detecting these interactions is called NMR spectrometer.

B. CHARACTERISTICS, PHYSICAL AND FUNCTIONAL

1. Repeatability:

   Given the same test parameters, the subsequent analysis of the same sample will be identical.

2. Quantitation:

To the chemist, NMR is indispensable for the characterization and quantitative estimation of all manner of complex organic molecules containing the nuclei ^{1}H, ^{2}H, ^{13}C, ^{31}p, ^{19}F, ^{15}N, ^{17}O, ^{11}B and ^{10}B.

3. Sensitivity:

For protons, ^{1}H, which are so ubiquitous in organic compounds, the state of development of NMR is such that it is possible to characterize and quantitate samples in the hundred-microgram range for components of molecular weight 400 to 500. The recent development of digital-sweep spectrometers, high-field superconducting spectrometers, time averaging techniques, and multiple pulse Fourier transform techniques will allow the sensitivity of the method to be extended by a factor of 10, and perhaps by a factor of 1000 with the last-mentioned technique.

4. Sample Preparation and Size:

NMR is a non-destructive technique requiring very little sample preparation. The sample is dissolved in an inert solvent from which it can easily be recovered, a valuable asset when little sample is available and other tests must be performed. Separation of a mixture is not required. Identification and quantitation may be made from a very impure compound, in contrast to IR spectra.

C. CHARACTERISTICS, OPERATIONAL

1. Time for Analyses:

After preparation of the sample, the average analysis time is 150 sec. to 5000 sec.

2. Training:

Anyone with a reasonable knowledge of organic compounds can learn to operate an instrument and to interpret spectra in one or two days.

3. Maintenance:

The usual nominal electronic ability is sufficient to provide the preventive maintenance required. Manufacturers have this service, and it is not costly. Annual maintenance costs do not exceed $1000.

The instruments require only 210 volts to operate. They must have a source of cooled water and an air-conditioned room for optimum performance.

D. COSTS

The cost of equipment runs from $25,000 to $200,000. The $25,000 equipment will do the spectra shown in this presentation. Manufacturers will run spectra and interpret them at a charge of $60 to $200 each. The cost is less, if one does their own spectral interpretation.

Varian is the only company providing this service on the West Coast; because of the backlog, there is a waiting period of one to two months. All other companies are on the East Coast, and the average waiting time is approximately one month.

II. NUCLEAR MAGNETISM

This section will describe the basic NMR effect (see attachment).

III. CHEMICAL APPLICATIONS OF NUCLEAR MAGNETISM

In NMR, there are two very important effects which are of use to chemists. These are the NMR chemical shifts and the nuclear spin-spin couplings.

The NMR chemical shift is determined by the extent of shielding of or the electron density about a nucleus. For protons, various chemical types have rather distinct resonance frequencies. This is useful in organic chemistry for establishing the structure of unknown molecules, analyzing mixtures, and testing the purity of a compound. The relative chemical shifts give a large amount of information about the very small differences of charge which exist on the various atoms or groups making up a neutral molecule.

The nuclear spin-spin couplings present a more subtle effect. As shown by the quantum mechanics of the interaction of nuclear spins with magnetic fields, a particular nucleus can have only certain orientations with the applied magnetic field. The spin-spin splitting is used to identify various kinds of chemical groups in molecules. The numerical values of spin-spin splittings in Hz can be used to establish the orientation of atoms in molecules and give information on the nature of different types of chemical bonds.

IV. NMR OF BARBITURATES

Some examples will be discussed which illustrate the characterization of certain drugs in the barbiturate series. There are well known ambiguities in the infrared (IR) spectroscopy of these drugs.

V. JPL USAGE OF NMR

Over the years, JPL has developed a capability in magnetic research to solve a range of problems involving propellants, polymer structure, basic chemical research on the structure of small molecules and analyses of returned lunar samples.

VI. POTENTIAL USAGE OF NMR IN CRIMINALISTICS

There has been a tremendous development in NMR spectroscopy in the last 10 years to the point where an NMR spectrum will be given the highest priority in the characterization of new or unknown organic chemical compounds. Today, NMR spectra are being offered as more definitive evidence than good elemental analyses.

VII. CONCLUSIONS AND SUMMARY

Nuclear magnetic resonance (NMR) spectroscopy is one of the newest and most spectacular techniques available to chemists for the elucidation of molecular structure and chemical analyses of organic molecules. NMR is a non-destructive technique requiring very little sample, which may be impure. The chemical shifts and the nuclear spin-spin couplings are two very important NMR effects which are of use to chemists. NMR can identify certain barbiturates which can not be unambiguously characterized by IR spectroscopy. Today, NMR spectra are more definitive evidence than elemental analyses in identifying new or unknown organic compounds.

There are a number of potential applications of nuclear magnetic resonance to problems faced by today's forensic chemist.

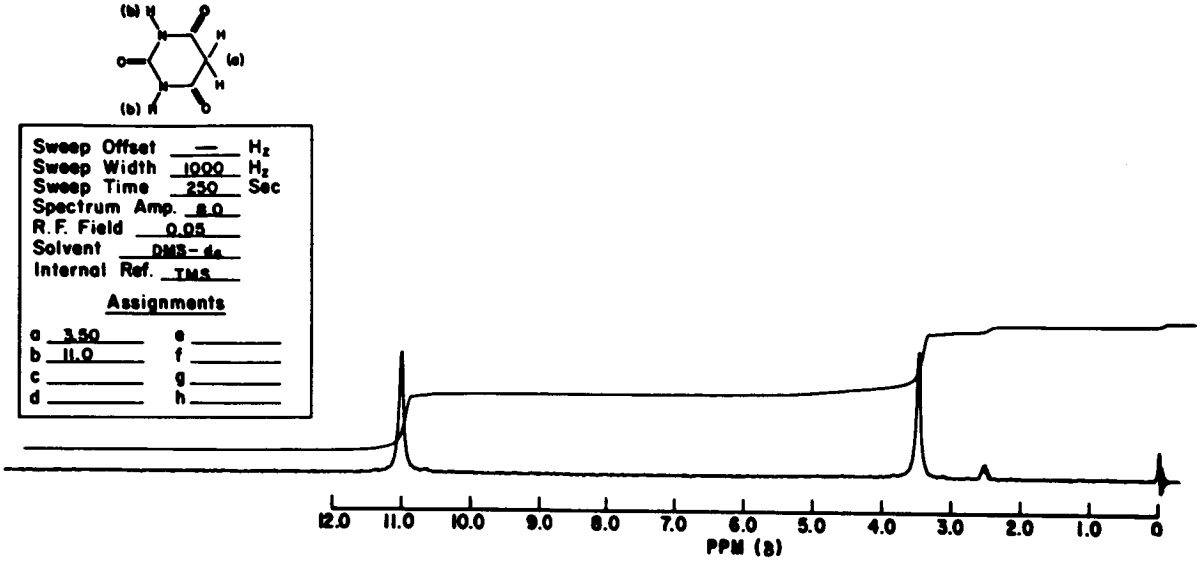


Fig. 2-1. PMR spectrum of barbituric acid

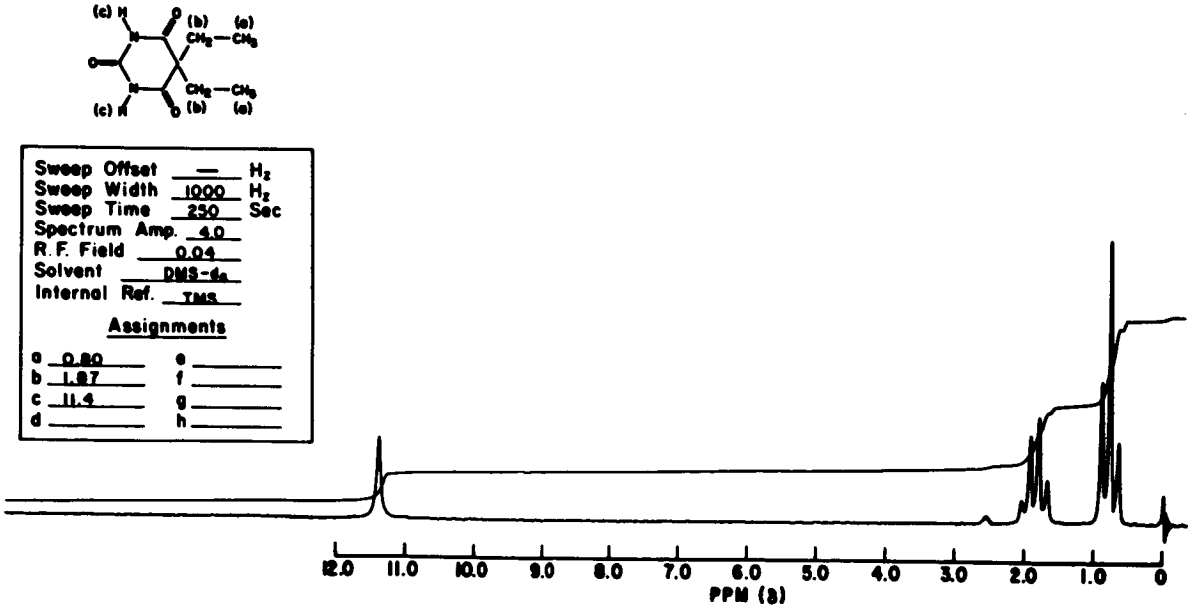


Fig. 2-2. PMR spectrum of 5, 5-diethylbarbituric acid

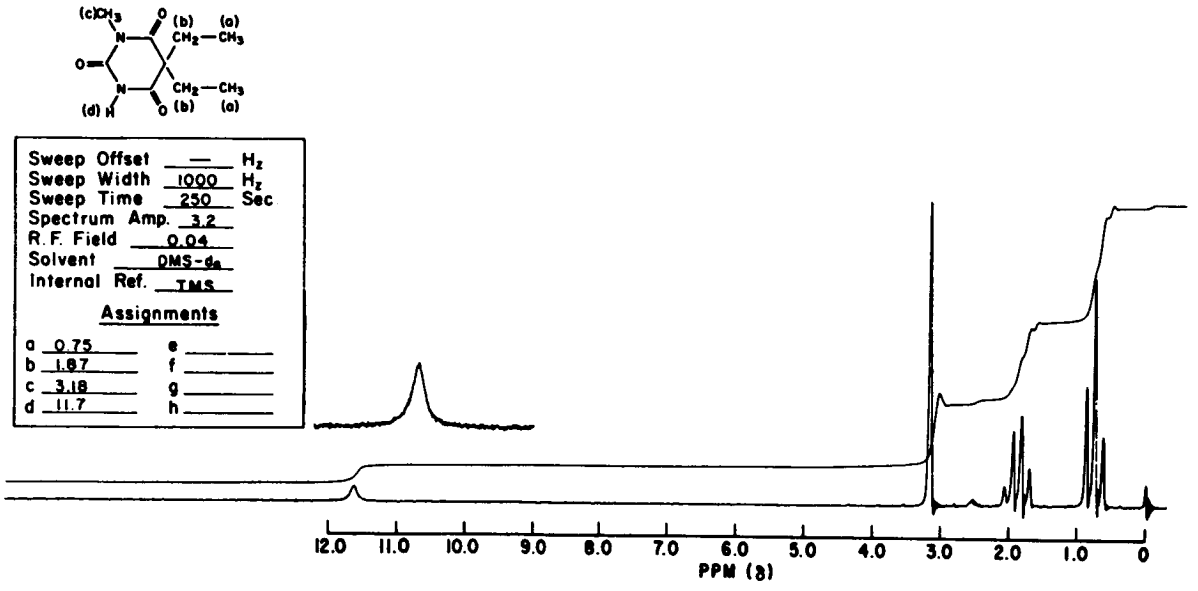


Fig. 2-3. PMR spectrum of 5, 5-diethyl-1-methylbarbituric acid

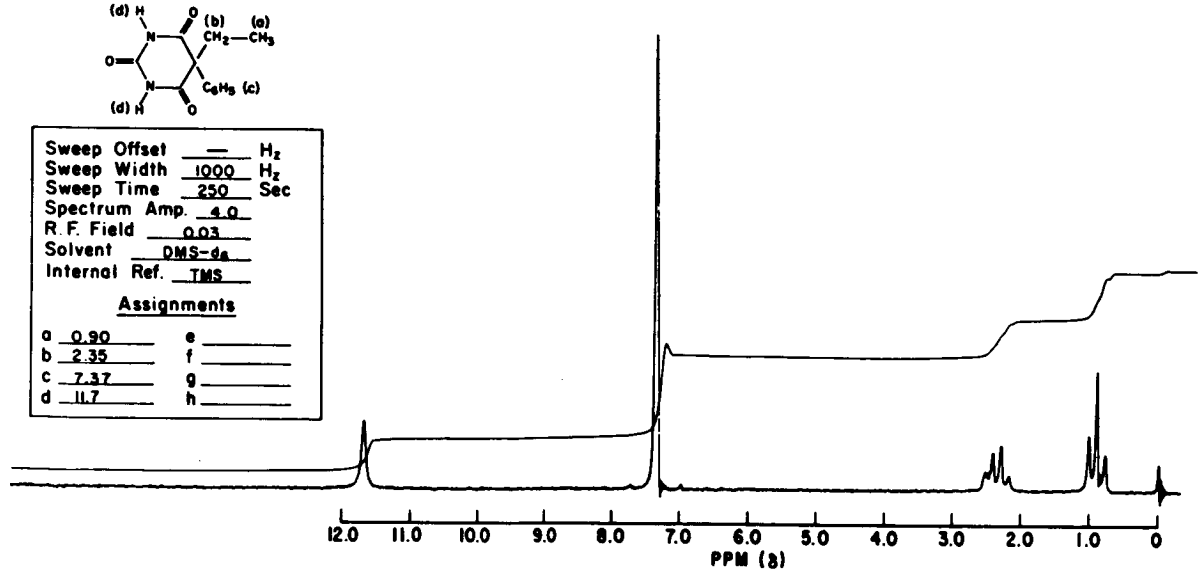


Fig. 2-4. PMR spectrum of 5-ethyl-5-phenylbarbituric acid

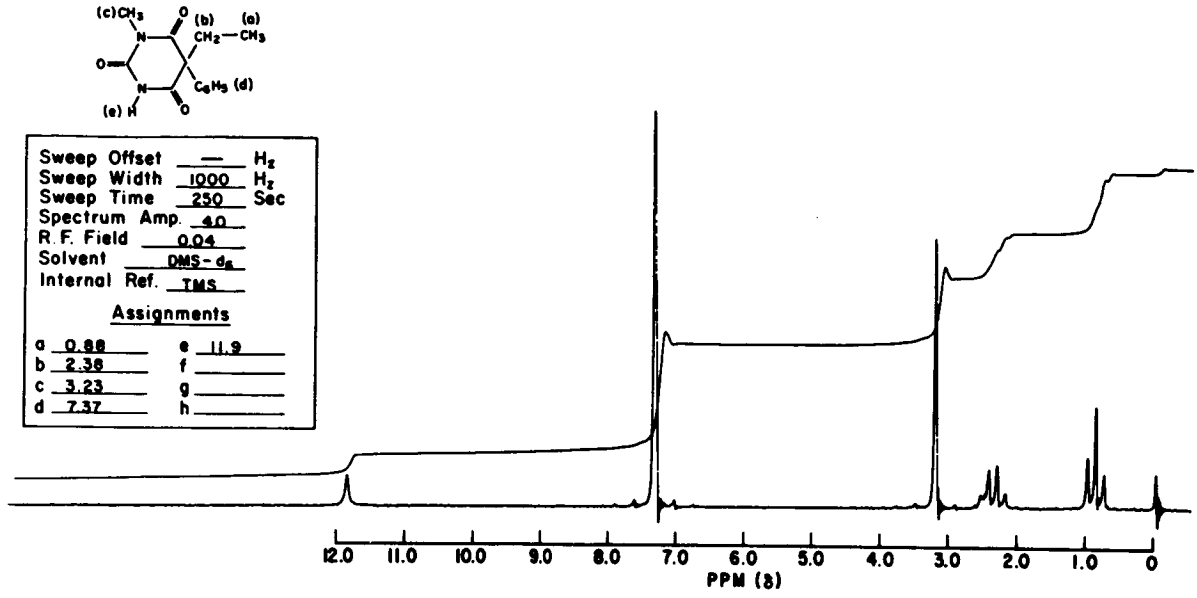


Fig. 2-5. PMR spectrum of 5-ethyl-1-methyl-5-phenylbarbituric acid

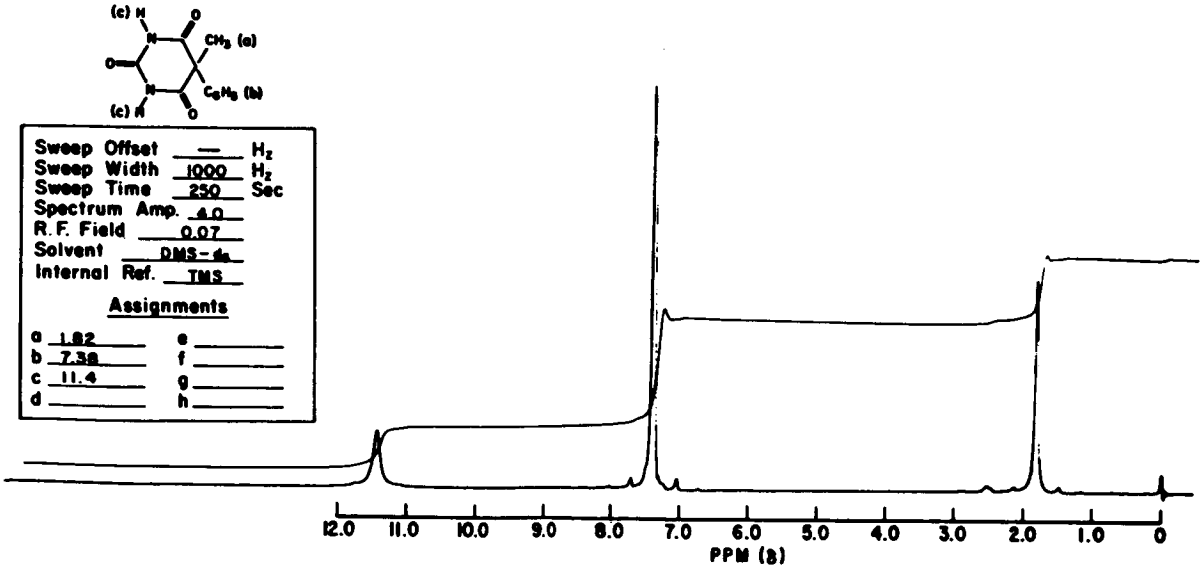


Fig. 2-6. PMR spectrum of 5-methyl-5-phenylbarbituric acid

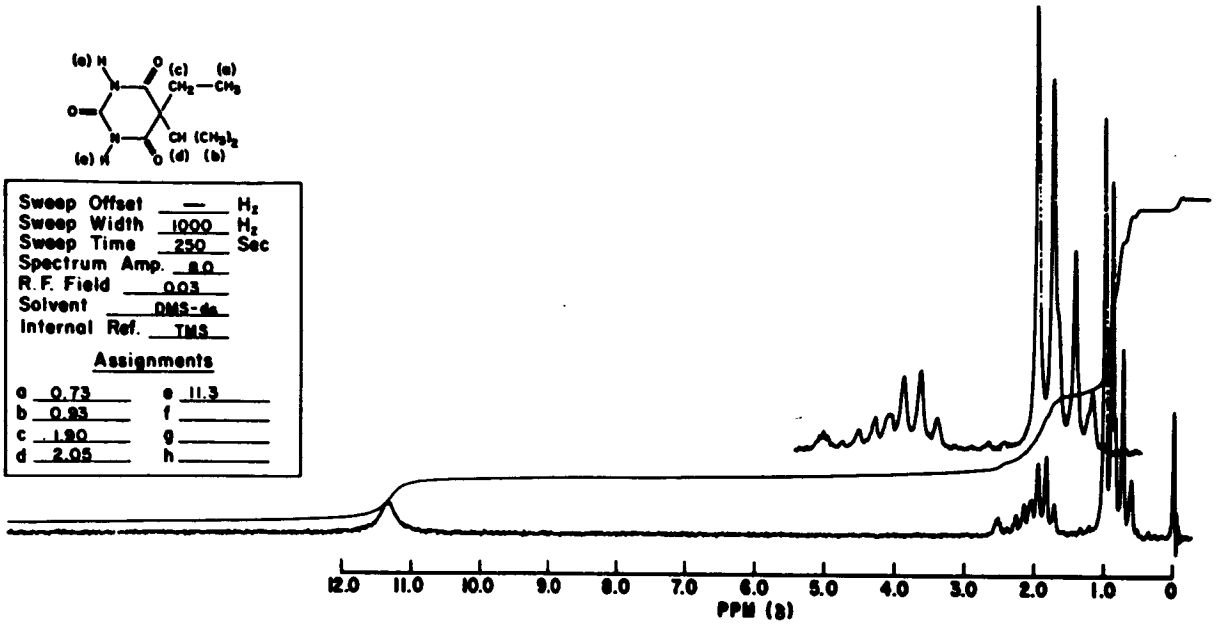


Fig. 2-7. PMR spectrum of 5-ethyl-5-isopropylbarbituric acid

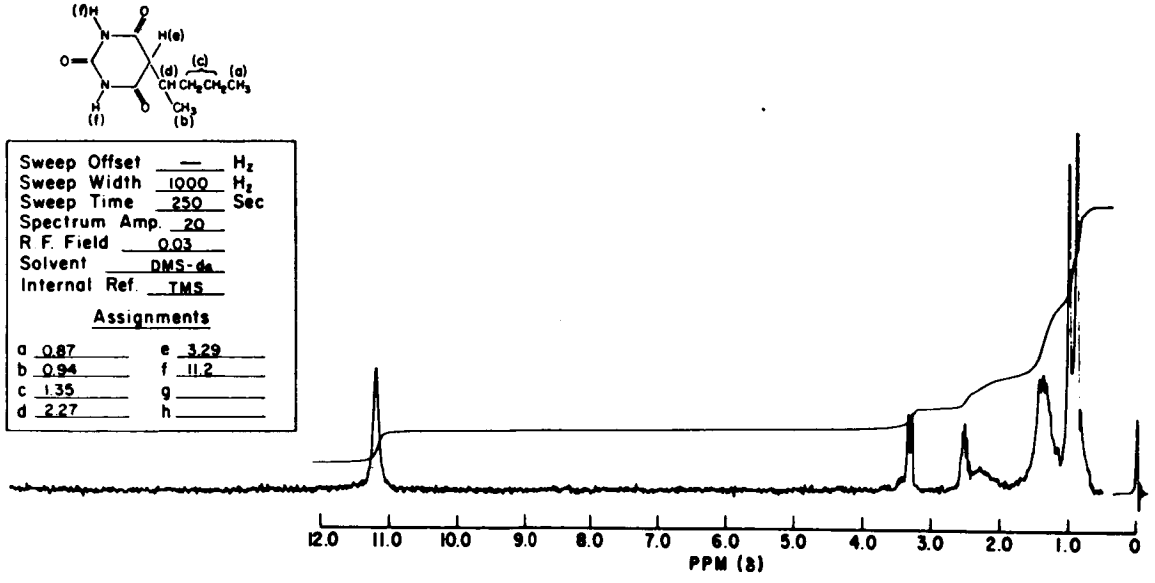


Fig. 2-8. PMR spectrum of 5-(sec-pentyl) barbituric acid

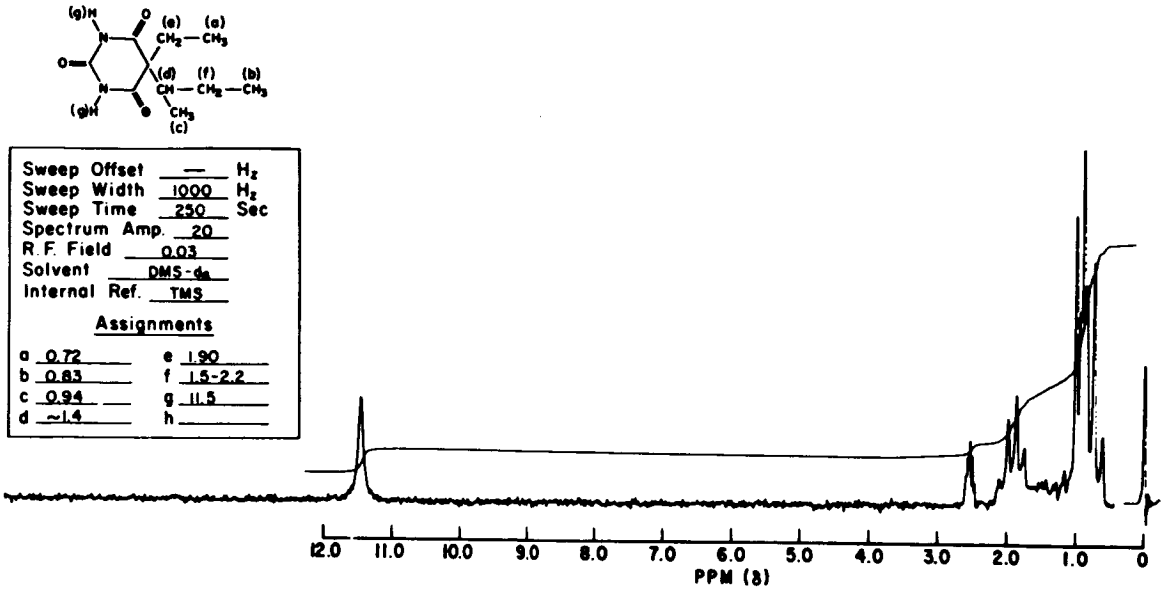


Fig. 2-9. PMR spectrum of 5-(sec-butyl)-5-ethylbarbituric acid

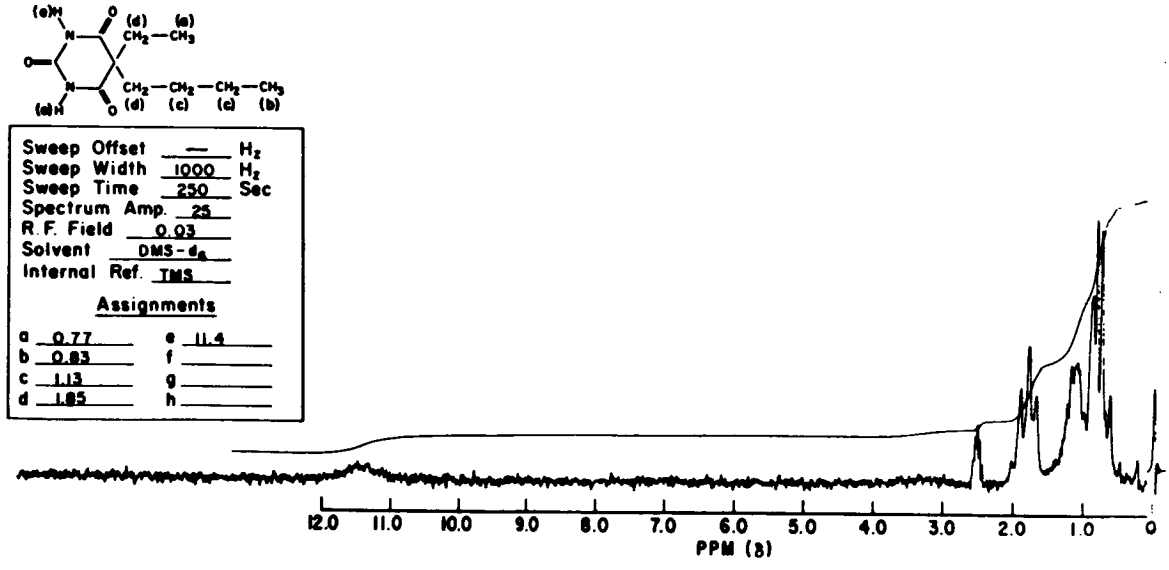


Fig. 2-10. PMR spectrum of 5-n-butyl-5-ethylbarbituric acid

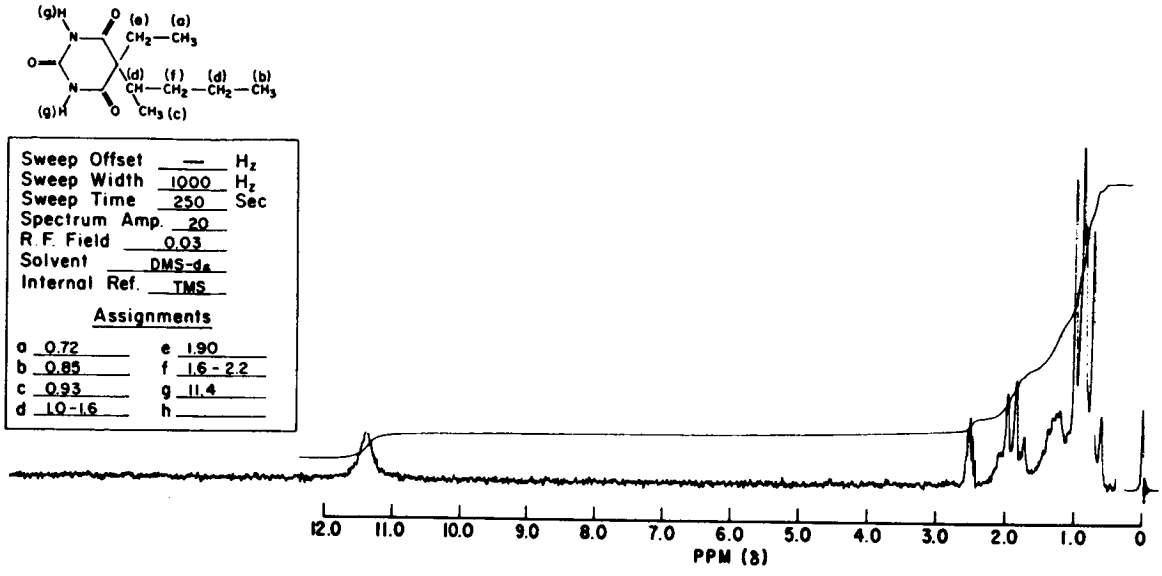


Fig. 2-11. PMR spectrum of 5-ethyl-5-(sec-pentyl) barbituric acid

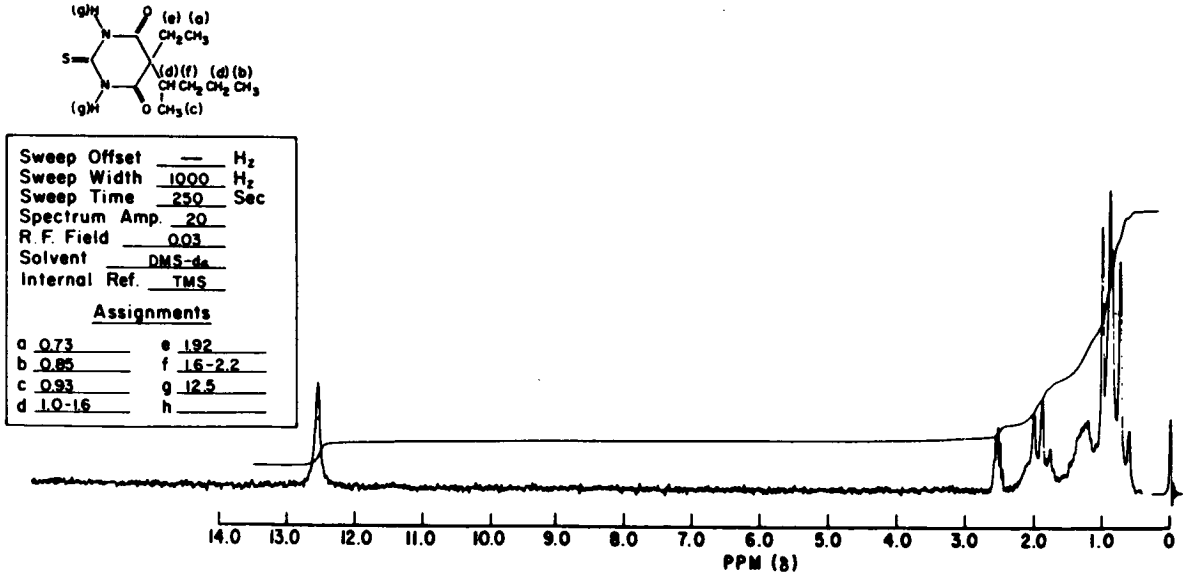


Fig. 2-12. PMR spectrum of 5-ethyl-5-(sec-pentyl) thiobarbituric acid

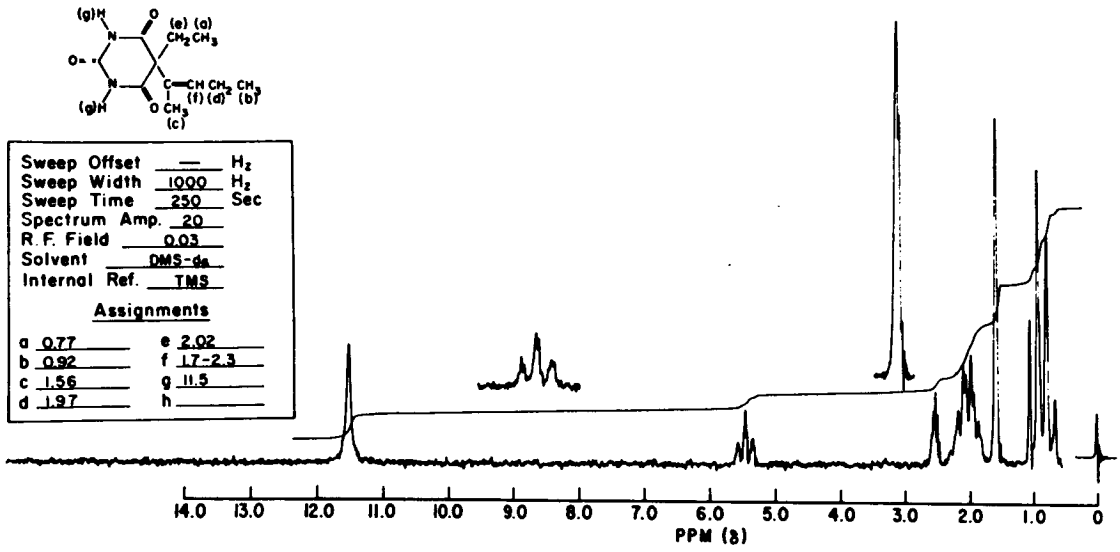


Fig. 2-13. PMR spectrum of 5-ethyl-5-(sec-pentenyl-2) barbituric acid

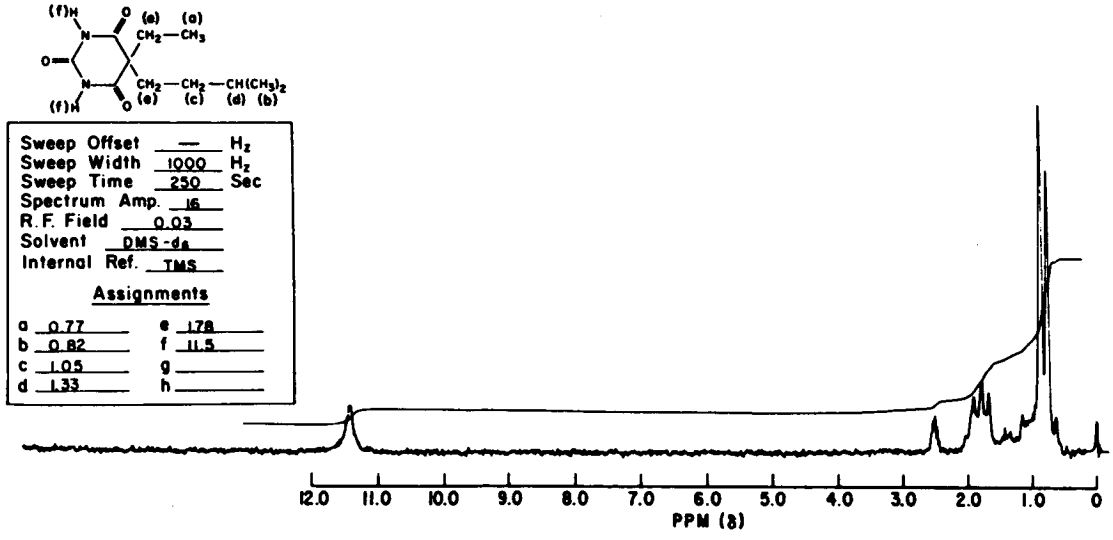


Fig. 2-14. PMR spectrum of 5-ethyl-5-(4'-methylbutyl) barbituric acid

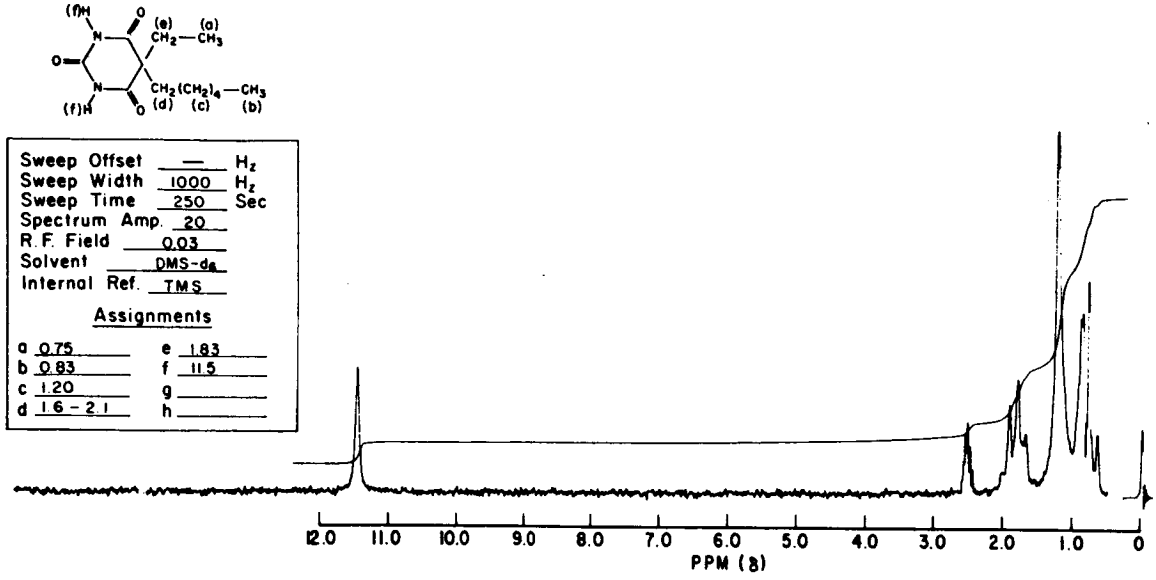


Fig. 2-15. PMR spectrum of 5-ethyl-5-hexylbarbituric acid

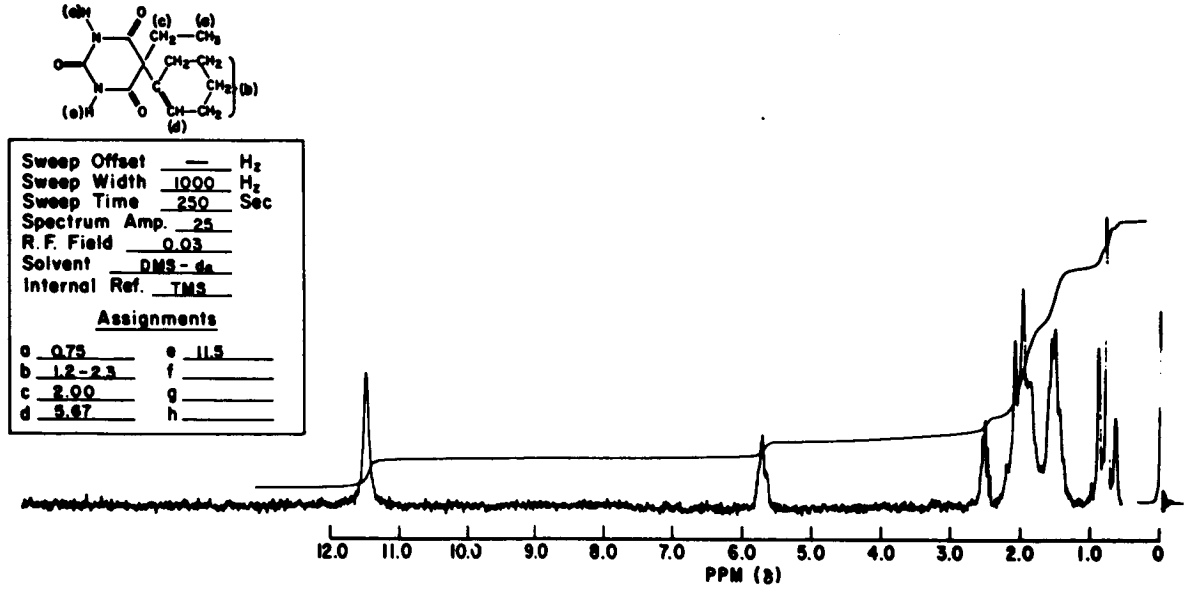


Fig. 2-16. PMR spectrum of 5-(1-cyclohexenyl-1)-5-ethylbarbituric acid

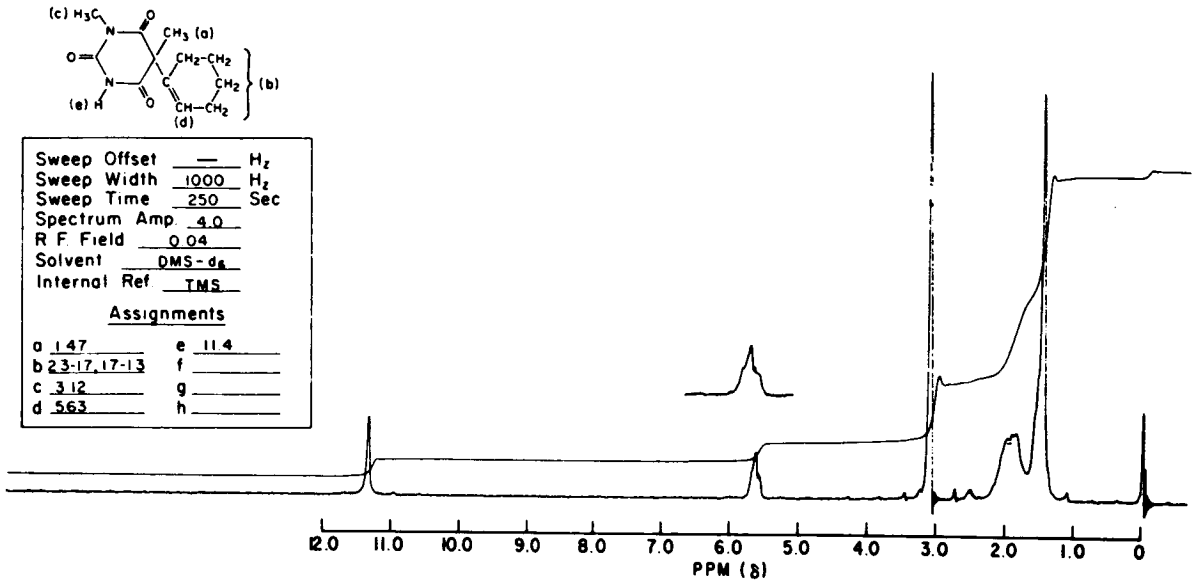


Fig. 2-17. PMR spectrum of 5-(1-cyclohexenyl-1)-1-methyl-5-methylbarbituric acid

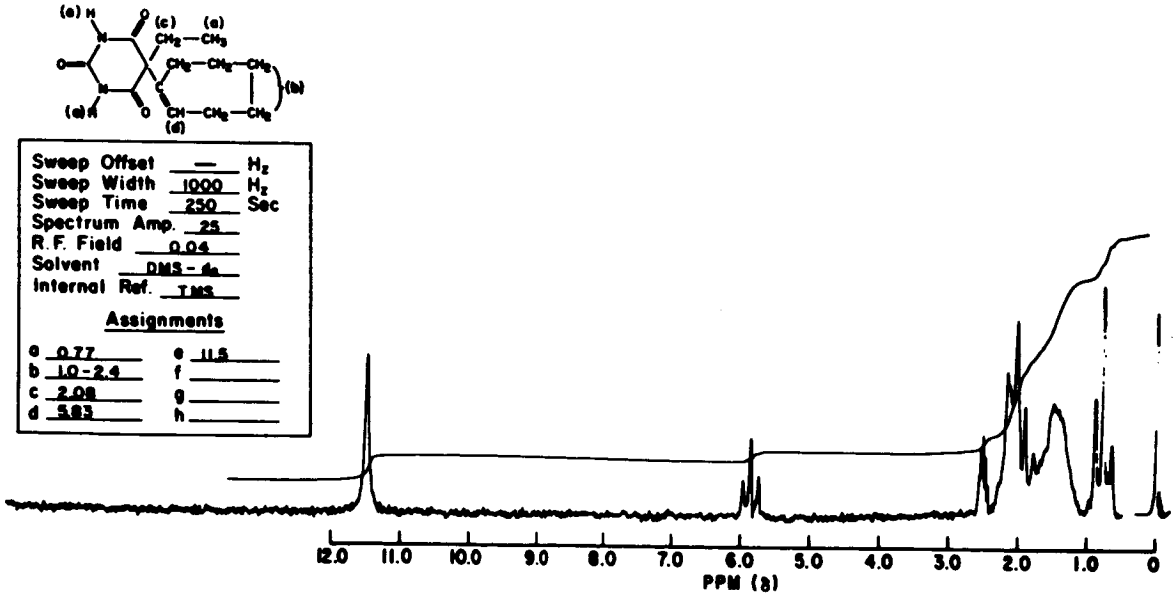


Fig. 2-18. PMR spectrum of 5-(1-cycloheptenyl-1)-5-ethylbarbituric acid

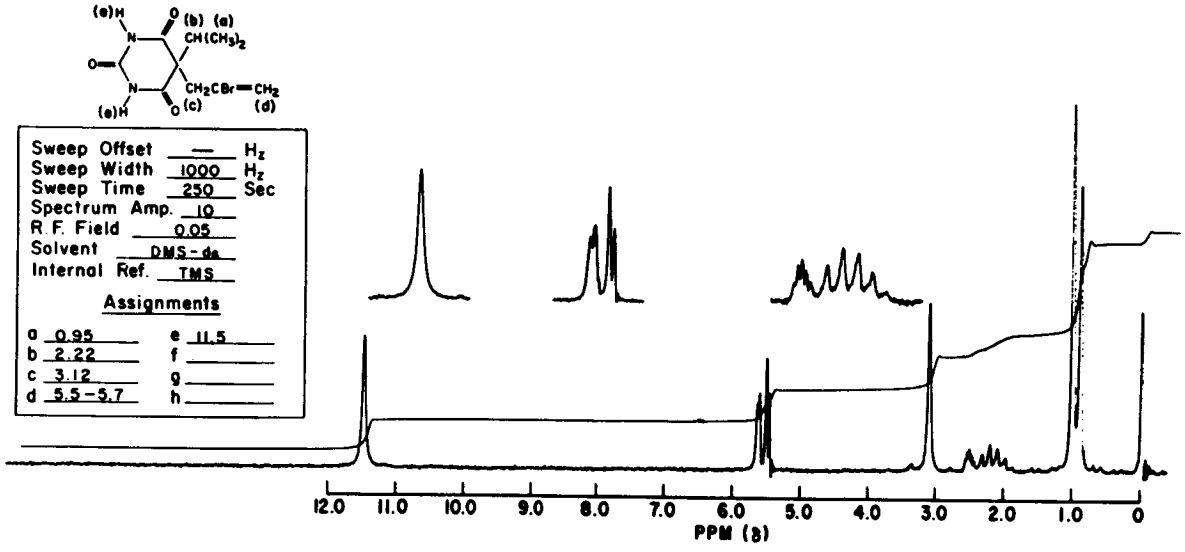


Fig. 2-19. PMR spectrum of 5-(2'-bromallyl)-5-isopropylbarbituric acid

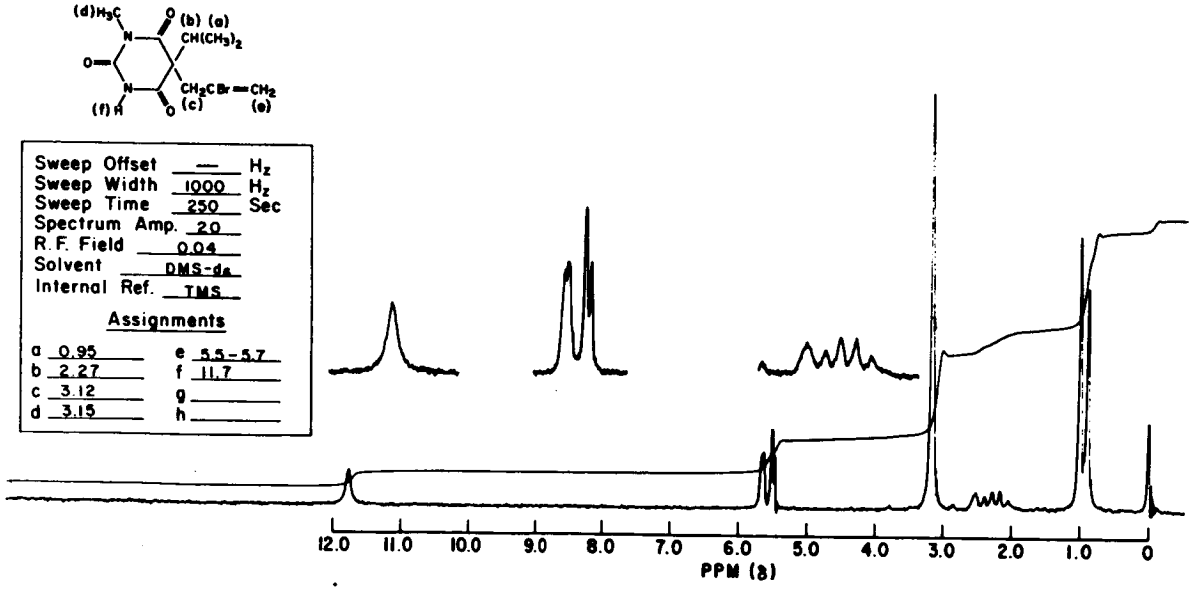


Fig. 2-20. PMR spectrum of 5-(2'-bromallyl)-5-isopropyl-1-methylbarbituric acid

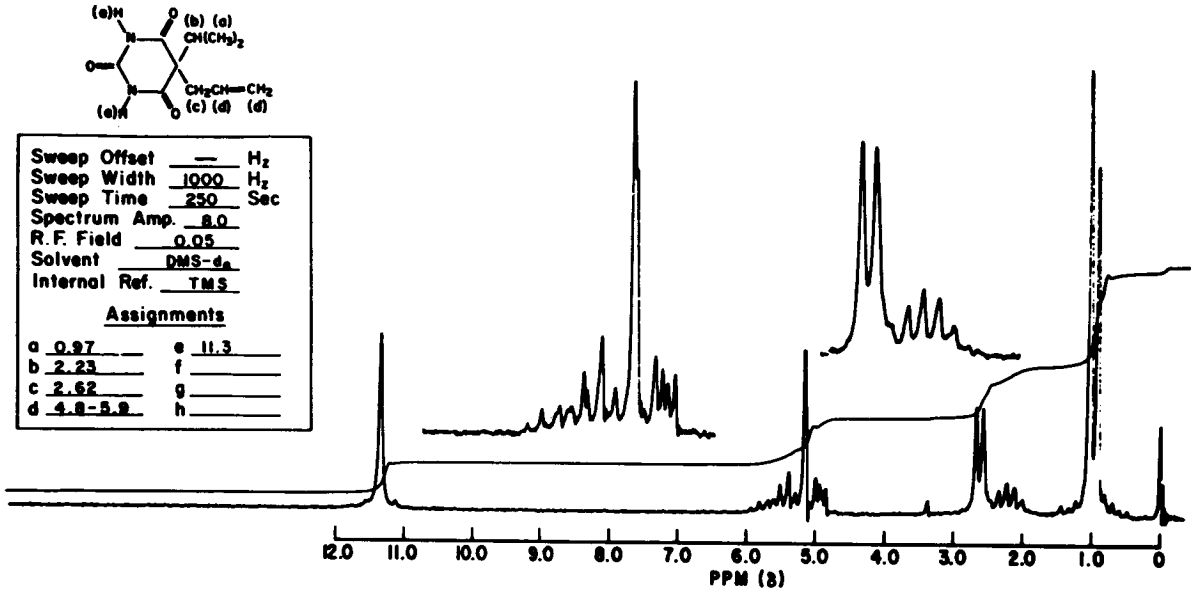


Fig. 2-21. PMR spectrum of 5-allyl-5-isopropylbarbituric acid

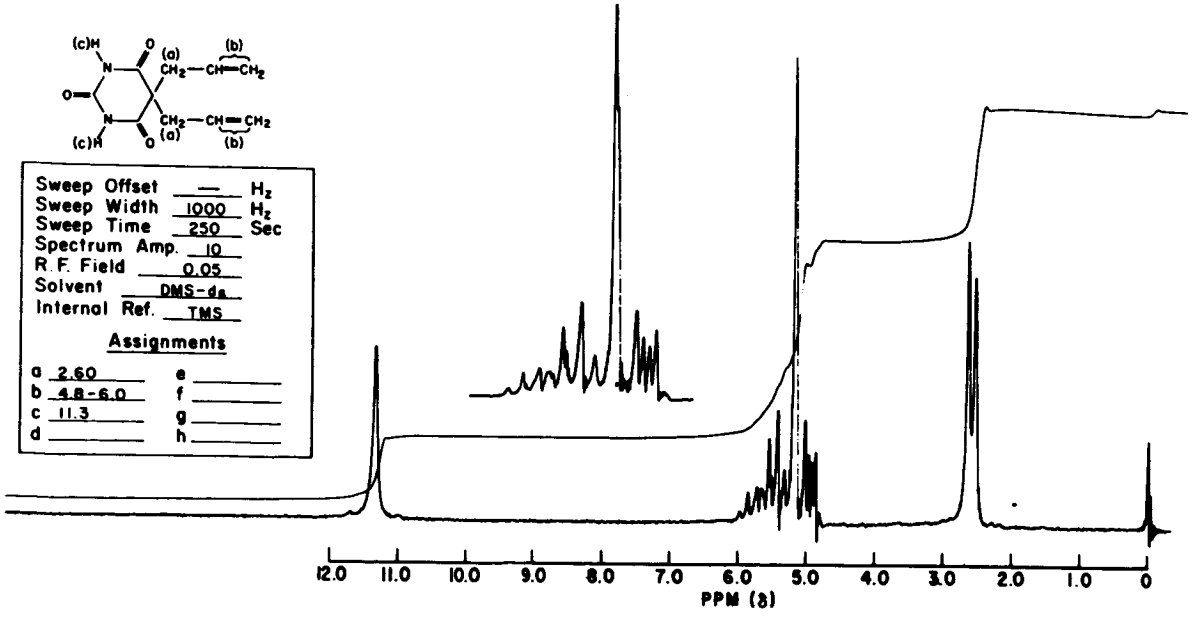


Fig. 2-22. PMR spectrum of 5, 5-diallylbarbituric acid

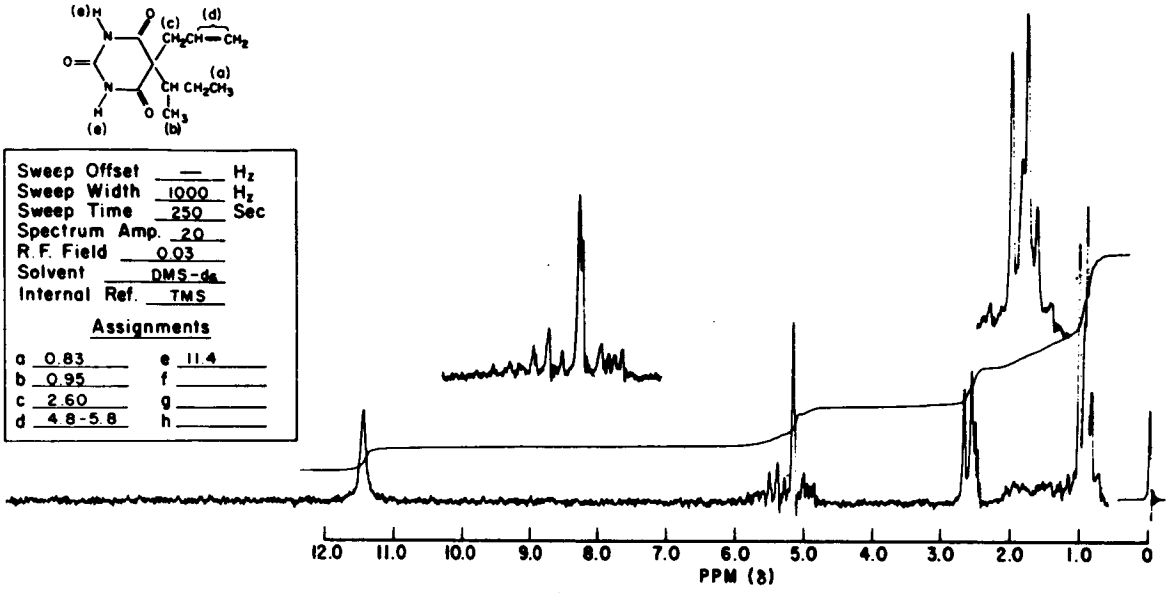


Fig. 2-23. PMR spectrum of 5-allyl-5-(sec-butyl) barbituric acid

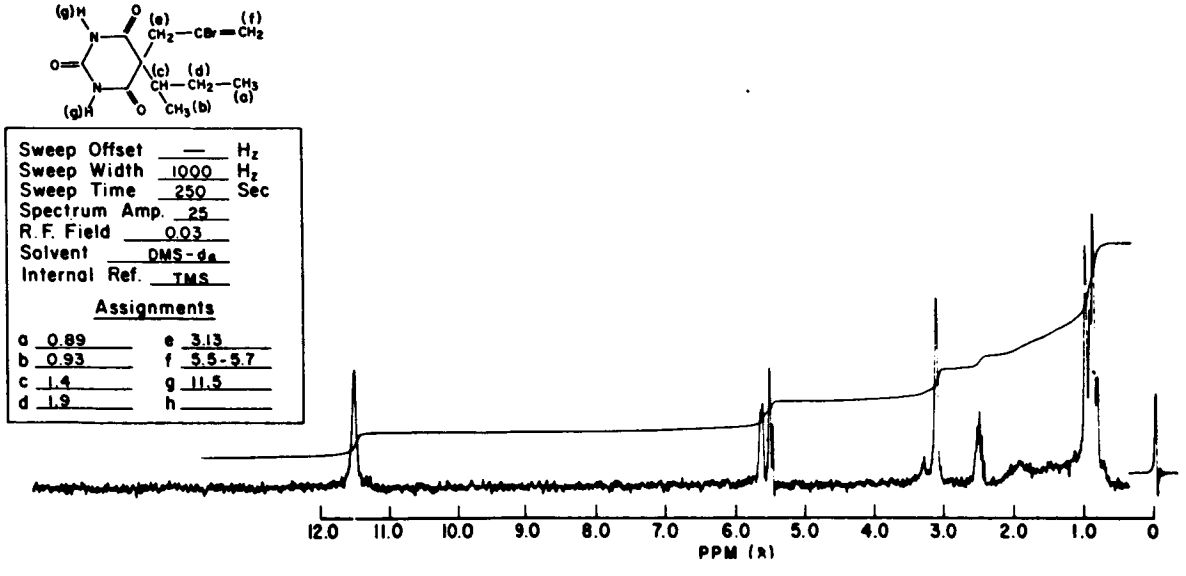


Fig. 2-24. PMR spectrum of 5-(2'-bromallyl)-5-(sec-butyl) barbituric acid

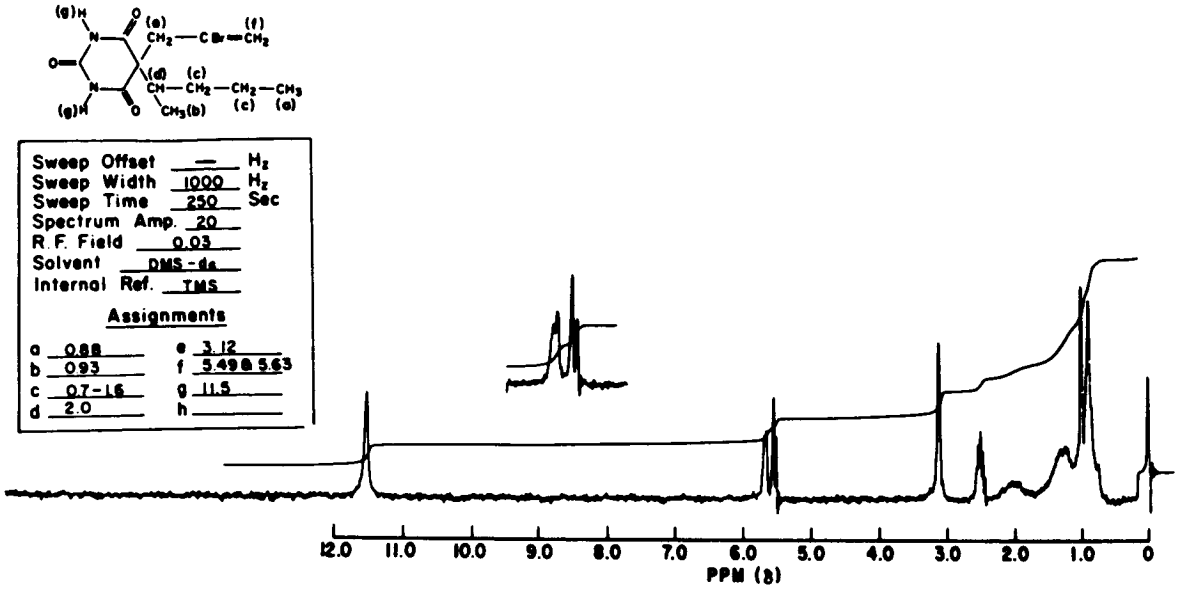


Fig. 2-25. PMR spectrum of 5-(2'-bromallyl)-5-(sec-pentyl) barbituric acid

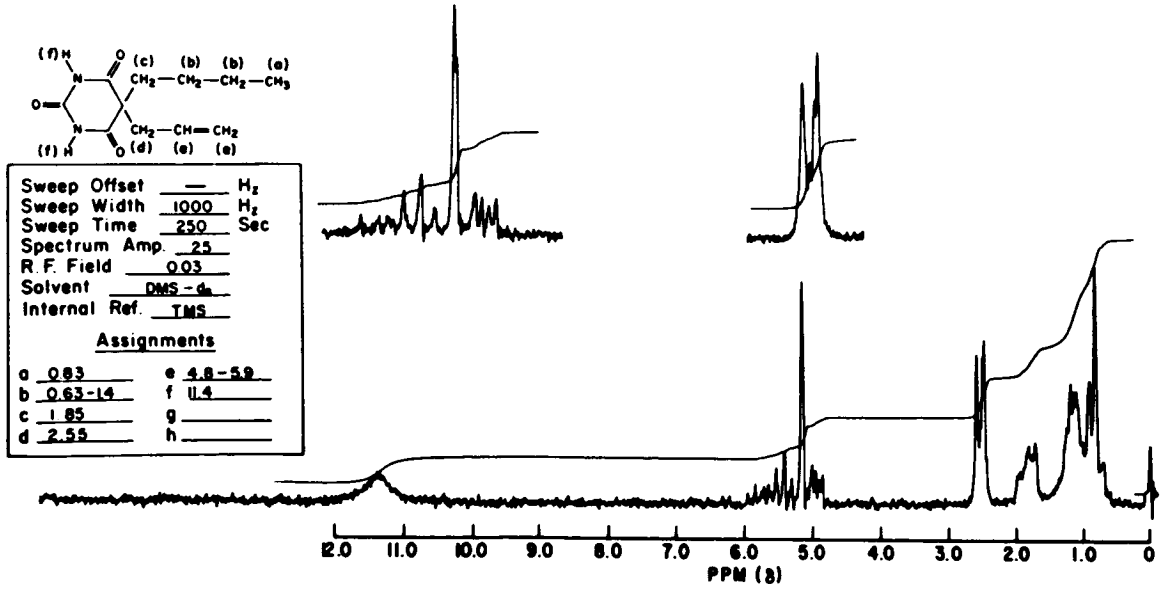


Fig. 2-26. PMR spectrum of 5-allyl-5-n-butylbarbituric acid

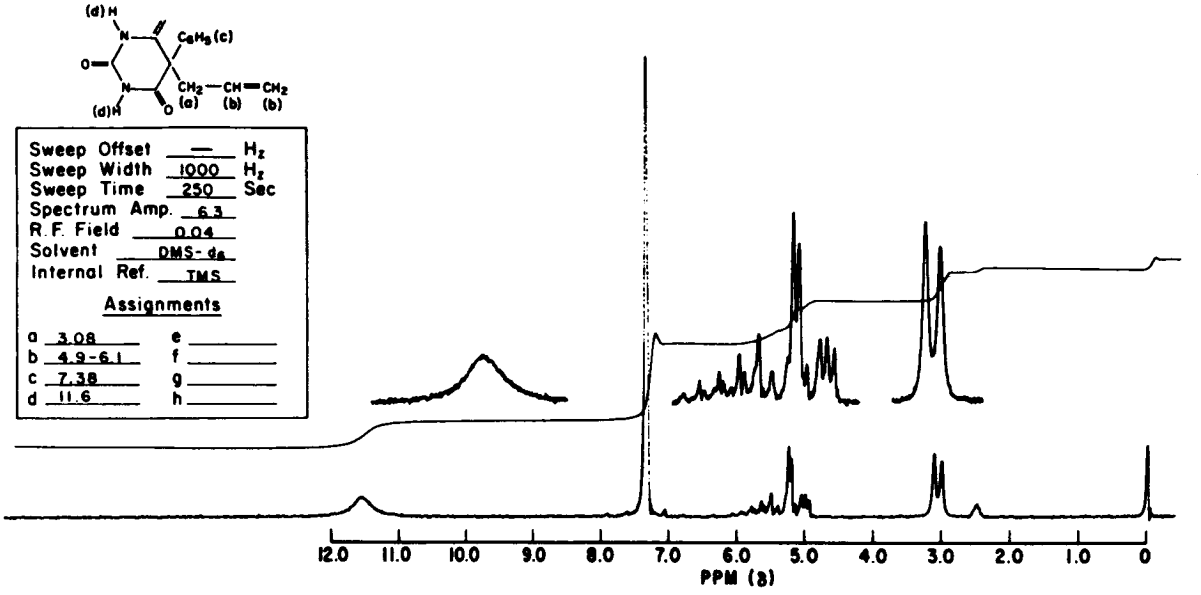


Fig. 2-27. PMR spectrum of 5-allyl-5-phenylbarbituric acid

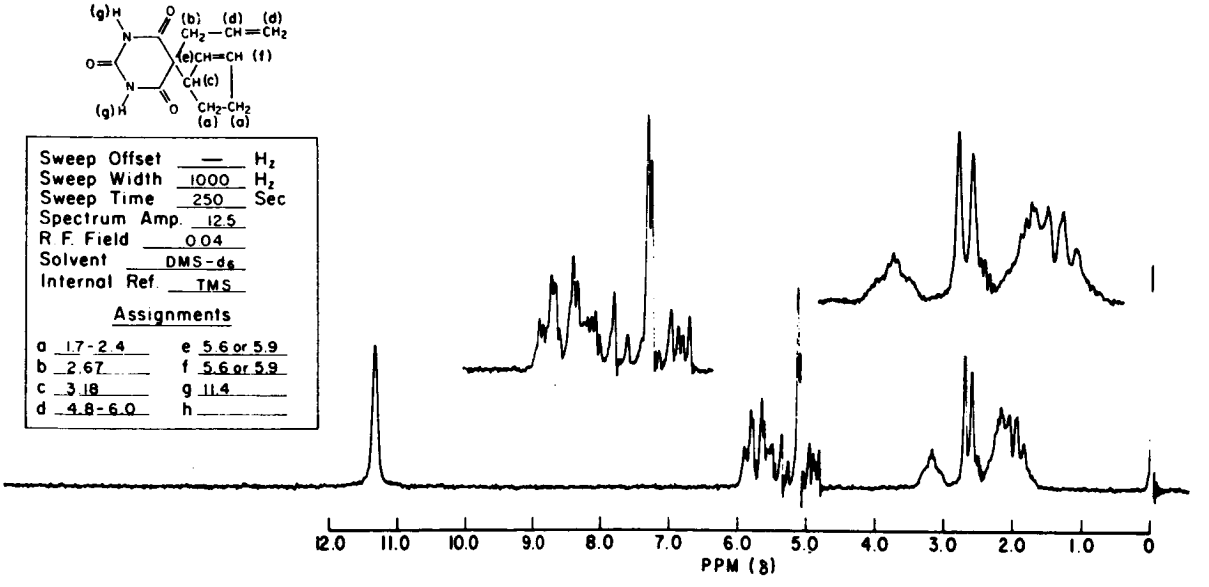


Fig. 2-28. PMR spectrum of 5-allyl-5-(1-cyclopentenyl-2) barbituric acid

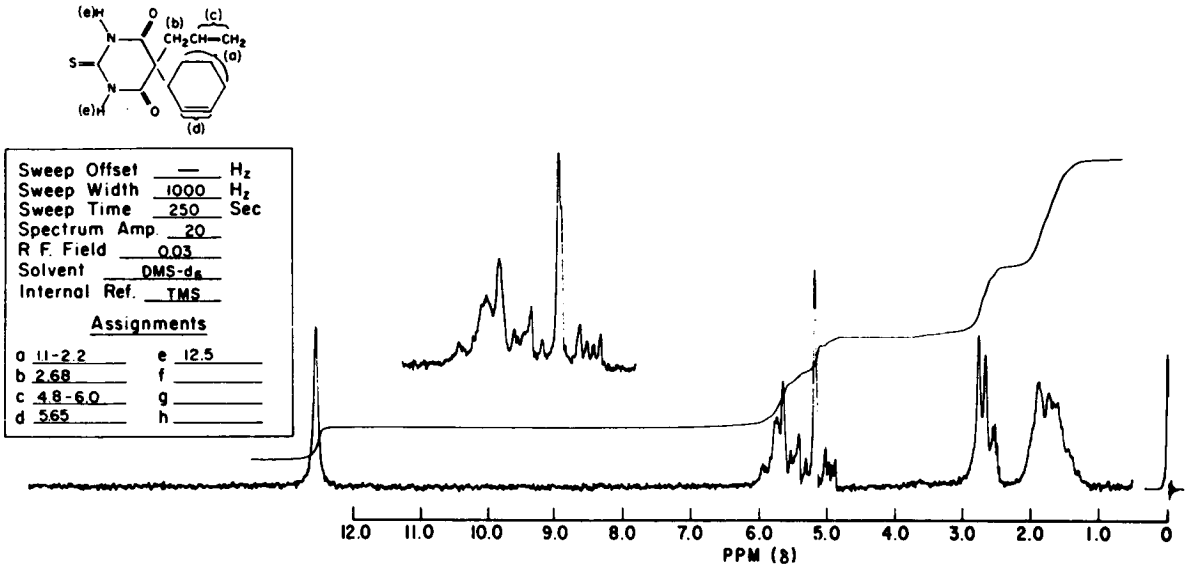


Fig. 2-29. PMR spectrum of 5-allyl-5-(1-cyclohexenyl-2) thiobarbituric acid

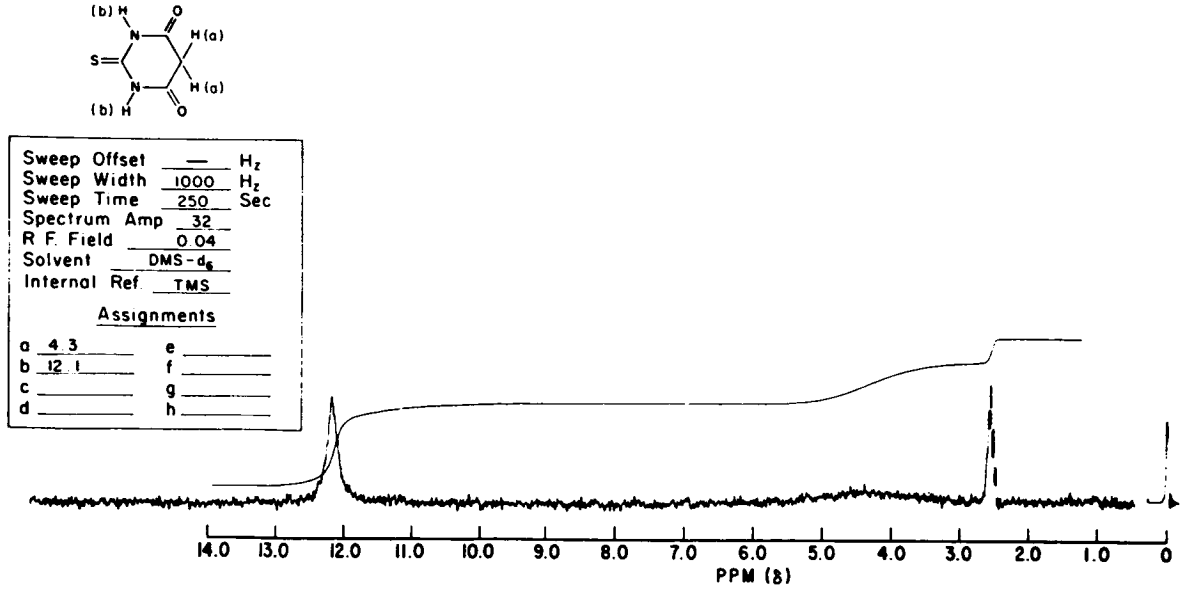
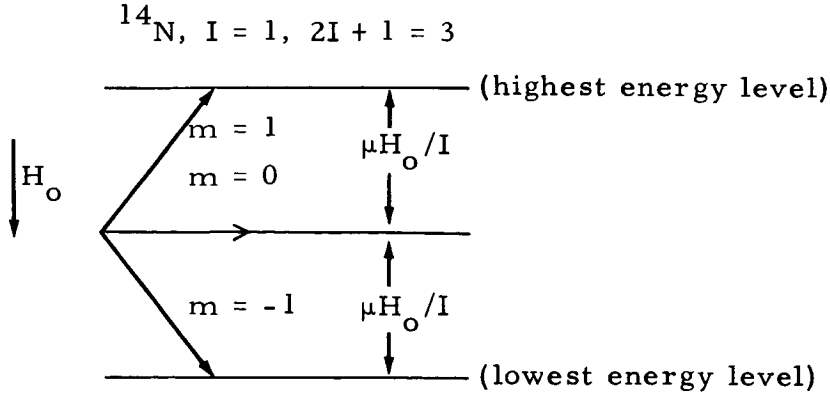


Fig. 2-30. PMR spectrum of 2-thiobarbituric acid

NUCLEAR MAGNETISM

Certain atomic nuclei, which are the seat of atomic positive charge, act as if they are spinning on their axes with a spin angular momentum of $I\hbar$ where I is the integral or half integral spin and $\hbar$ is Plank's constant (6.625×10^{-27} erg sec) divided by 2π. Arising from the spinning nuclear charge is a magnetic field of the dipole type whose strength is described in terms of a nuclear magnetic moment whose maximum component is μ. Identical magnetic nuclei when placed in a magnetic field of strength H_o precess at a frequency given by $\omega = \gamma H_o$ where ω is the angular frequency in radians/sec ($\omega = 2\pi\nu$ where ν is the frequency in cycles) and γ is the gyromagnetic ratio which is the ratio of the nuclear magnetic dipole moment μ to the spin angular momentum $I\hbar$. In a magnetic field nuclei with a given spin I are found to distribute themselves among 2I + 1 levels. Each level has a definite energy, represents a specific magnetic dipole vector component along the H_o direction and can be described by one of the 2I + 1 magnetic quantum numbers m that range from I to -I in value. The difference of energy between two adjacent levels is given by $\mu H_o/I$. The precession frequency in every level is the same. This situation is illustrated for ^{14}N, which has I = 1, in the adjacent diagram



The distribution taken between the 2I + 1 levels of a group of nuclei of spin I is determined at thermal equilibrium with the surroundings or lattice by the Boltzmann relation

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/\kappa T}$$

where N_i and N_j are the numbers in levels i and j and i being the level of higher energy, κ is Boltzmann's constant (1.3804×10^{-16} erg deg^{-1}), T is the absolute temperature and $E_i - E_j = (m_i - m_j)\mu H_o/I$. If this latter expression is small then the excess population between two levels can be expressed as

$$n_{\text{excess eq.}} = \frac{N}{2I + 1} \frac{(m_i - mj)\mu H_o}{I} \frac{1}{\kappa T}$$

where N is the total number of nuclei. By applying a radio frequency field of the nuclear precessional frequency to a group of nuclei in a magnetic field it is possible to induce transitions (or cause a nucleus to change its m value by +1) between the 2I + 1 unequally populated levels. Such absorption of energy results in a transition from a state of lower energy to a state of higher energy. It is possible to upset the Boltzmann distribution. For non-equilibrium populations it is possible to define a spin temperature which can be much higher than that of the lattice. When the relative population of two nuclear spin levels are disturbed from equilibrium they tend to return to the lattice temperature by transitions downward (m = -1 processes) with a characteristic time T_1 which is called the spin-lattice relaxation time. The equation which describes the return to equilibrium between two levels is

$$(n_{\text{excess eq.}} - n_{\text{excess}}) = (n_{\text{excess eq.}} - n)e^{t/T_1}$$

where $n_{excess\ eq.}$ is the excess in the lower level at thermal equilibrium, n is the excess in the lower level at some time t, n_{excess} is the excess in the lower level existing initially (t = o) after the system has been disturbed by incident radio frequency energy, and T_1 is the spin-lattice relaxation time. At thermal equilibrium for two levels there will always be an excess in the lower energy level. It is possible by absorption of a pulse of energy to have the largest population in the upper of two levels. In this case n_{excess} would have a negative value in the equation above and also n could have both negative and positive values.

Problems

1. The isotope of boron, ^{10}B, present in 18.83% has a spin I = 3. What are the set of nuclear magnetic quantum numbers for this nucleus?
2. The isotope of oxygen $^{17}0$, present in 0.037%, has a spin I = 5/2. How many possible components can an assemblage of $^{17}0$ nuclei exhibit in a magnetic field?
3. A proton, ^{1}H, (I = 1/2) is placed in a magnetic field of 14.095×10^3 gauss. Calculate its resonance frequency in this field based on the experimental evidence that its resonance frequency in a 1.00×10^3 gauss field was observed to be 4.2577 megacycles/sec (1 megacycle/sec = 10^6 cycles/sec).
4. Calculate the gyromagnetic ratio for ^{1}H from the data in the previous problem.
5. Using the approximation that $e^x = 1 + x$ for small x, estimate the excess number of nuclei in the lowest energy level (m = -1) for a group of

3.00×10^{18} of ^{14}N nuclei (I = 1) at 300°K and in a magnetic field such that the ^{14}N precession frequency is 3.076 megacycles/sec.

6. Calculate at what temperature the ratio of the populations in the two levels for a group of ^{1}H nuclei (I = 1/2) in a field of 1.00×10^{4} gauss will be 1:2 (upper level:lower level) ($e^{.692} = 2.00$).

7. With a large pulse of radio frequency energy, the relative populations of a group of 3.00×10^{18} of ^{13}C nuclei (I = 1/2) are inverted such that the ratio of the number of nuclei in the upper state (m = 1/2, highest energy) to that in the lower state is 2:1. If T_1 for these ^{13}C nuclei is 1000 seconds, how long will it be before the populations of the two levels are equal? The lattice temperature is 300°K. For these ^{13}C nuclei $\mu H_o/I$ is 1.00×10^{-19}. It is useful to know that the $\log_e 10 = 2.303$ and $\log_e 2.76 = 1.015$.

THERMOANALYTICAL METHODS

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I. INTRODUCTION

Thermal analysis is an analytical technique used to identify and characterize all varieties of organic and inorganic materials. In thermal analysis, the temperature of a sample is controlled, and some physical or chemical property is monitored. Initially, thermal analysis methods were used for the identification and characterization of minerals. Chemists used thermal methods to characterize high molecular weight polymers. This field has developed rapidly during the last 20 years. See Fig. 3-1 for some present applications of this technique and the temperature ranges with which they are most often associated.

A. MODERN THERMAL ANALYSIS SYSTEM

Any measurement of thermal properties must be made by a transducer which monitors the property and converts the information into an electrical signal which is capable of being amplified and recorded.

All of the transducers used in the various thermal analysis techniques require a programmer to regulate temperature, an amplifier for boosting the transducer output, and a recorder on which to plot the signal (see Fig. 3-2).

Various thermal techniques are:

1. Differential Thermal Analysis (DTA)
2. Thermogravimetric Analysis (TGA)
3. Thermomechanical Analysis (TMA)
4. Electrical Thermal Analysis (ETA)
5. Effluent gas detection and analysis
6. Thermoluminescence

II. CHARACTERISTICS

A. PHYSICAL AND FUNCTIONAL

1. Repeatability:

   The repeatability of Thermoluminescence and of TGA in soils is

   $$X^2 \leqq 2.$$

2. Specificity:

   Thermal methods are good for individualization; they are not generally specific.

3. Sensitivity:

   Thermal techniques are limited to solid samples.

4. Sample Preparation and Size:

   Sample sizes should be between 5 and 20 mm and should be subdivided to 125 to 250 mesh for reproducibility. Impurities are not a factor.

B. OPERATIONAL CHARACTERISTICS

1. Analysis Time:

   Thermoluminescence, after radiation of the material, requires about 3 min analysis time. Most of the other methods require 1 to 2 hr.

2. Training:

   The equipment is easy to operate. A chemist would have no problems, and a technician could be trained on the job in 2 wk.

3. Maintenance:

   Maintenance problems are directly related to the sophistication of the equipment. There are no special utility requirements except the Thermoluminescence (TOL) which requires a Cobalt 60 source. Other than standard procedures required for dealing with 60 Cobalt, there are no special safety problems connected with the use of thermal analysis instruments.

C. COSTS

Equipment costs vary from $4500 for a simple Thermogravimetric Analyzer up to $35,000 for a complete apparatus. Most universities are equipped for thermal analysis, and the equipment can be leased from most manufacturers on a rent purchase plan. There are no large operating expenses.

III. THERMOGRAVIMETRIC ANALYZER

A. DESCRIPTION

TGA is a technique for continuously monitoring the weight of a sample as a function of temperature or as a function of time at a specified temperature.

This technique has been used to study quantitatively weight losses associated with dehydration and decomposition phenomena. It can also be used in the study of weight gains such as oxidation, hydration, and hydride formation. Any reaction resulting from interaction of the sample with a gas or evolving a gas can be investigated by this method. A diagram of a thermogravimetric balance utilizing an electromagnetic transducer is shown in Fig. 3-3.

B. APPLICATIONS

The applications of TGA in identifying and characterizing materials are discussed in this section. A few sample illustrations are:

1. Differentiation of Soil Samples by TGA (Fig. 3-4).

2. TGA Reproducibility of a Soil Sample (Fig. 3-5).

3. Various Western Soils (Fig. 3-6).

4. Quantitative Determination of Components in a Clay Mixture:

TGA is a rapid means of determining quantitatively the amount of a certain mineral in a mixture. A prerequisite is to have the mineral undergo a known weight loss over a narrow enough temperature range to avoid overlap. Figure 3-7 shows the use of TGA in the analysis of a kaolinite-hectorite mixture.

5. Estimation of Plasticizer Content:

TGA provides a rapid determination of the amount of plasticizer in a high polymer system, if the plasticizer is completely volatized prior to the polymer decomposition, and if there is no interaction between the two. This analysis, using other techniques, usually is tedious, if not hopeless. Figure 3-8 shows the results of the TGA technique.

6. Effect of Flame Retardent on Cotton Decomposition:

TGA scans can be used to follow the path of thermal degradation of flame-resistant textiles. See Fig. 3-9 for scans of untreated aminized cotton and the same material treated with bromendic anhydride.

IV. DIFFERENTIAL THERMAL ANALYZER (DTA)

A. DESCRIPTION

DTA is a differential temperature monitor employing a differential thermocouple arrangement of two thermocouples wired in opposition. One thermocouple is placed in the sample to be analyzed and the other is placed in an inert reference material which will undergo no thermal transformations over the temperature range being studied. When the sample and reference material temperatures are equal, the net voltage output is zero. When the temperatures differ, the net voltage differential reflects this difference. A plot of the differential temperature, ΔT, as either a function of temperature or time, is known as a thermogram. Figure 3-10 is a diagram of the DTA apparatus.

The block type DTA cell is a metal block in which 3 wells have been drilled. The center well contains a cartridge heater controlled by the programmer. Glass or quartz tubes containing sample or reference material are placed in the outer wells. Thermocouples are then inserted into the tubes with their junctions positioned in the center of the comparison materials (see Fig. 3-11).

The cup cell sampling system consists of platinum sample and reference cups resting on the tops of two analytical thermocouples and supported by thin thermocouple insulators. The platinum-platinum 13% rhodium thermocouples

are situated 6 mm apart and are separated from the heat source by an "air" space. The atmosphere in this space can be controlled through connections on the Du Pont 900 TA console. This allows an analyst to evacuate or purge the space with an inert gas or to introduce a reactive gas. Figure 3-12 shows a cup cell cross section.

The heart of the Differential Scanning Calorimeter (DSC) cell is a thermoelectric disc that consists of a Constantan plate with raised platforms for placement of a sample pan and a reference pan. A chromel wire is welded at the center of each platform, providing a thermocouple junction in direct contact with the bottom of each pan for measurement of temperature differential. An Alumel wire is welded at the center of the sample platform. This provides a Chromel-Alumel thermocouple junction for determining the temperature of the sample (see Fig. 3-13).

B. APPLICATIONS

1. Effect of Sample Weight on Resolution:

   The thermogram of a large 53.53 mg sample is poorly resolved, while that of a small 0.14 mg sample shows good resolution (see Fig. 3-14). The thermogram of the smaller sample was made at 20 times greater sensitivity.

2. Figure 3-15 illustrates the effect of atmosphere on calcium oxalate monohydrate. $Ca\ C_2\ O_4 \cdot H_2O$ decomposes in three stages corresponding to loss of water of hydration (150-200°C), dissociation into calcium carbonate and carbon monoxide (400-500°C), and decomposition into calcium oxide and carbon dioxide (675-775°C). The ease of atmosphere control provided by the cup cell system allows the investigator to quickly gather significant information on sample-atmosphere interactions.

3. Detection of Transitions and Impurities at High Temperatures:

   Figures 3-16, 3-17, and 3-18 (in series) shows the differential thermal analysis data obtained on an impure iron sample during a heat-cool-reheat sequence. The high temperature capabilities of this cell are illustrated by the melting endotherm (6) occurring at 1533°C. The ability to program cool allows the investigator to introduce known thermal histories in studying steels, alloys, and other materials.

4. Baseline Compensation Circuit:

   DSC cells as received from the factory always have uniformly sloping baselines, and therefore it is easy to obtain horizontal baselines through compensation. The Baseline Compensation Circuit employed with the DSC cell is illustrated in Fig. 3-19. Compensation is proportional to the sample temperature and is

independent of heating rate/recorder sensitivity or shift. The compensated baseline will apply to an external time-base recorder.

5. Figure 3-20 shows the straight horizontal baseline obtained with the DSC cell. This figure is an exact tracing of a thermogram made at ΔT sensitivity. The investigator can confidently interpret any deviation from such a baseline and can easily determine melting points and planimetering of peak areas.

V. THERMOMECHANICAL ANALYZER

A. DESCRIPTION

A Thermomechanical Analyzer (TMA) uses a Linear Variable Differential Transformer (LVDT) as a mechanical transducer. The LVDT generates an electrical signal which is directly proportional to the deflection of an iron core in respect to a null position. A quartz probe resting on top of the sample is connected directly to the iron core. The circled area of Fig. 3-21 is an expanded view of the penetration probe resting on a sample.

This module measures coefficients of expansion, softening ranges, glass transition temperatures, and many of the properties commonly measured by dynamic mechanical testing techniques.

B. APPLICATIONS

1. Linear Coefficient of Expansion from Slope of TMA Curve:

   Expansion measurements are extremely sensitive and can be used to study a variety of phenomena. Figure 3-22 shows the high sensitivity of the TMA in measuring the expansion of aluminum. Film samples can be layered in order to make expansion measurements.

2. Detection of Transitions in Thin Coatings by Penetration:

   When using means other than TMA to examine materials in the form of coatings and films, it is often necessary to remove the coating by scraping. This imparts unwanted thermal history to the sample. With TMA, films and coatings can often be examined on the substrate. Figure 3-23 shows a penetration run on polythylene coated paperware.

3. Figure 3-24 shows cure of coatings by TMA.

VI. ELECTRICAL THERMAL ANALYSIS (ETA)

The electrical conductivity of most materials will vary as a function of temperature. Using the technique of ETA, this change in conductivity can be continuously monitored using electrodes.

VII. EFFLUENT GAS DETECTORS

Effluent Gas Detectors can be used in conjunction with the previously mentioned transducers. Hot wire, flame ionization, and thermistor detectors are frequently employed. The modern trend in treating effluent gas is to analyze it, not just detect it. Gas, and thin film chromatography, and mass spectrometry are recent techniques in effluence analysis.

VIII. THERMOLUMINESCENCE (TOL)

A. DESCRIPTION

Thermoluminescence is the emission of light produced by heating a solid to a temperature below that of incandescence.

The solid is first exposed to ionizing radiation which produces a cloud of electrons within the lattice structure. Some of these electrons are trapped in imperfections and vacancies in the crystal lattice, and these escape with the emission of light when the temperature is raised to supply the necessary amount of kinetic energy (see Fig. 3-25 for a block diagram of the glow-curve apparatus).

B. APPLICATIONS

Any nonconductor or dielectric solid should give a glow curve. Figure 3-26 shows the glow curve of a thermoluminescent crystal measured simultaneously with a thermal bleaching curve.

IX. CONCLUSIONS AND SUMMARY

Thermal analysis techniques are those techniques in which the temperature of a sample is controlled, and some physical or chemical property is monitored. The temperature can either be varied with time or held constant.

Originally used by mineralogists to identify and characterize minerals and by chemists to characterize high molecular weight polymers, thermal analysis today spans all varieties of organic and inorganic materials.

This same technology which was successfully used in the space program to analyze lunar soil can be successfully used in the crime laboratory as an aid to criminalistics in analyzing all types of evidence materials.

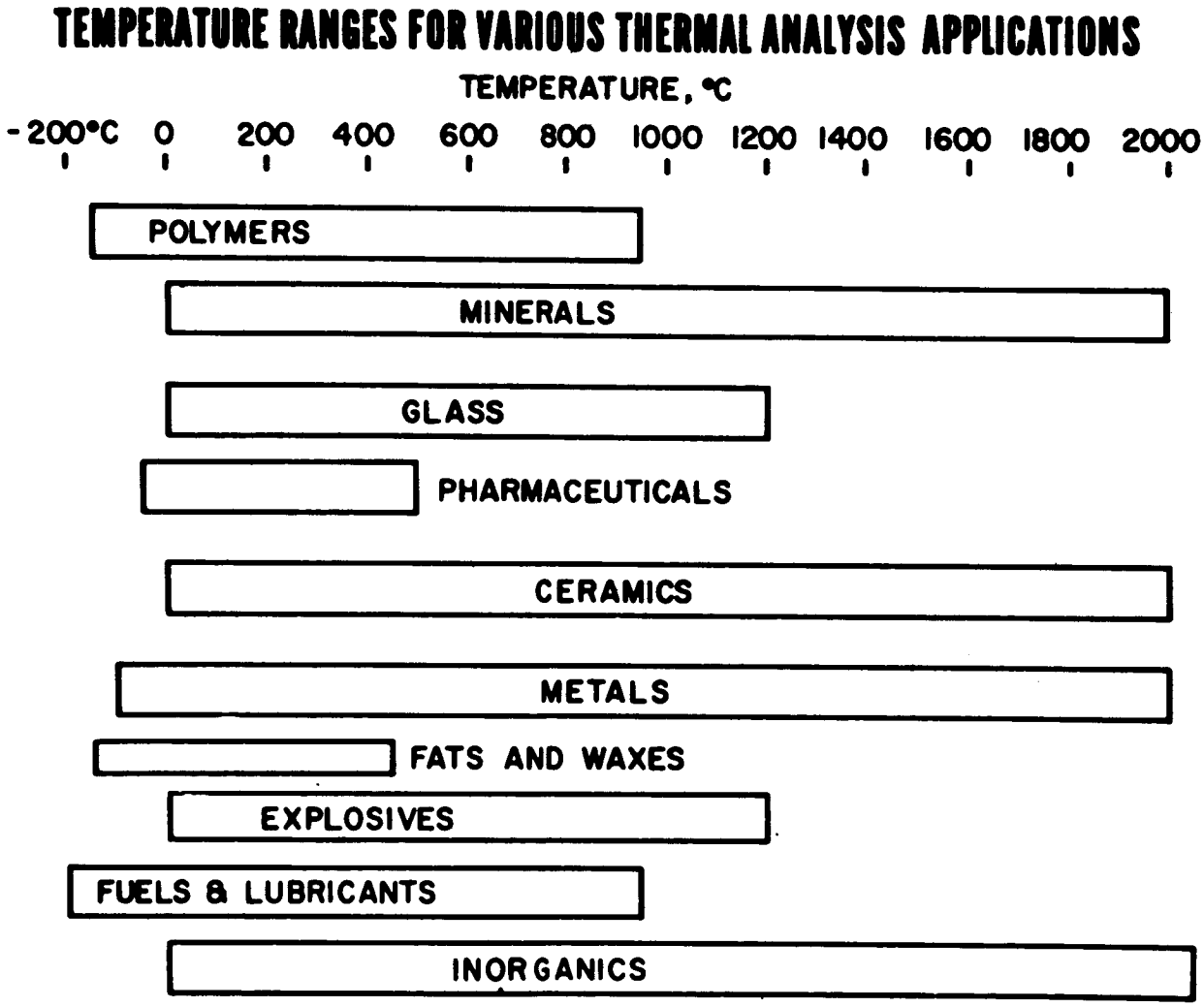
TEMPERATURE RANGES FOR VARIOUS THERMAL ANALYSIS APPLICATIONS
TEMPERATURE, °C
-200°C
0
200
400
600
800
1000
1200
1400
1600
1800
2000
POLYMERS
MINERALS
GLASS
PHARMACEUTICALS
CERAMICS
METALS
FATS AND WAXES
EXPLOSIVES
FUELS & LUBRICANTS
INORGANICS

Fig. 3-1

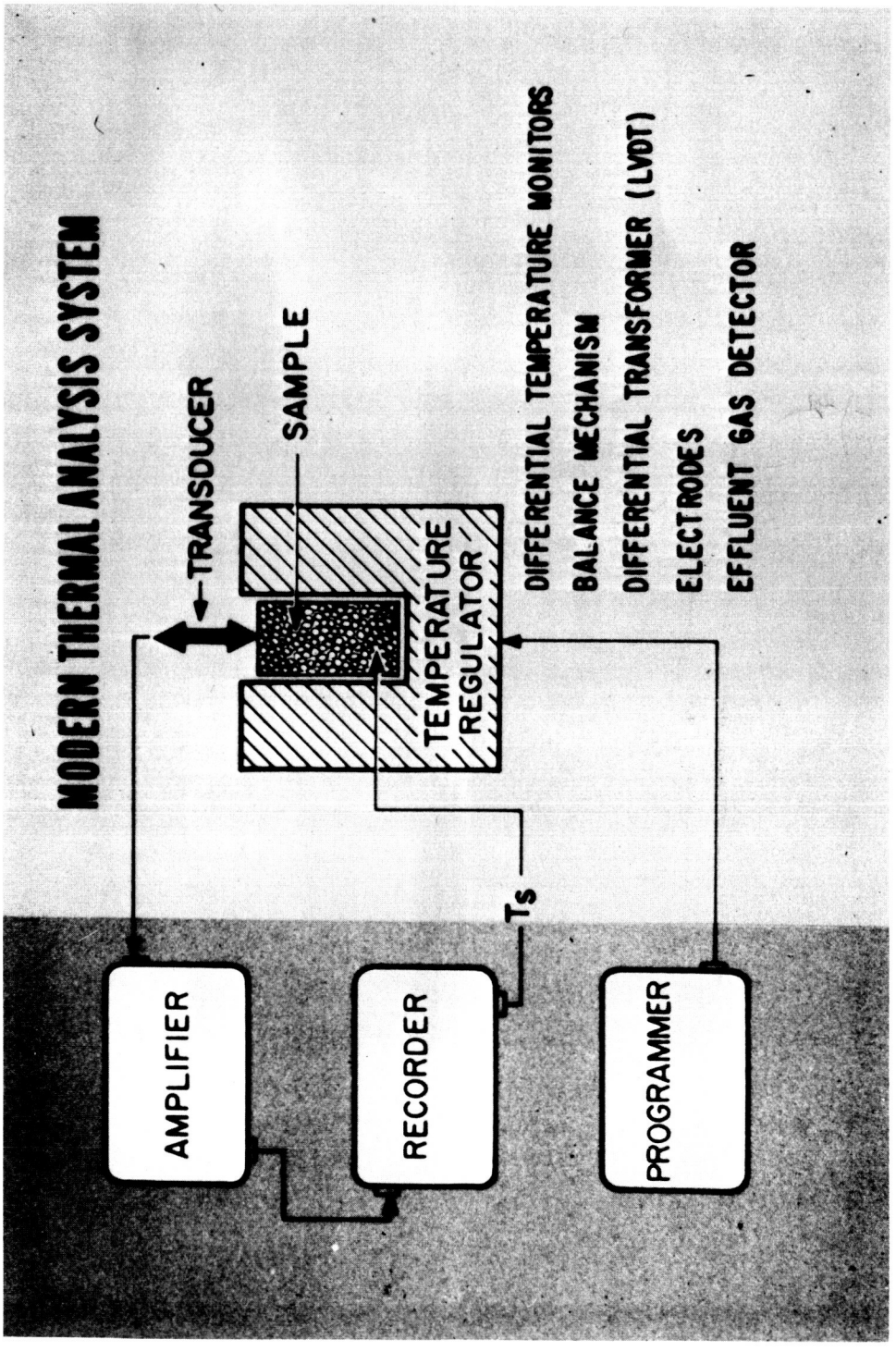
MODERN THERMAL ANALYSIS SYSTEM
TRANSDUCER
SAMPLE
TEMPERATURE REGULATOR
DIFFERENTIAL TEMPERATURE MONITORS
BALANCE MECHANISM
DIFFERENTIAL TRANSFORMER (LVDT)
ELECTRODES
EFFLUENT GAS DETECTOR
Ts
AMPLIFIER
RECORDER
PROGRAMMER

Fig. 3-2

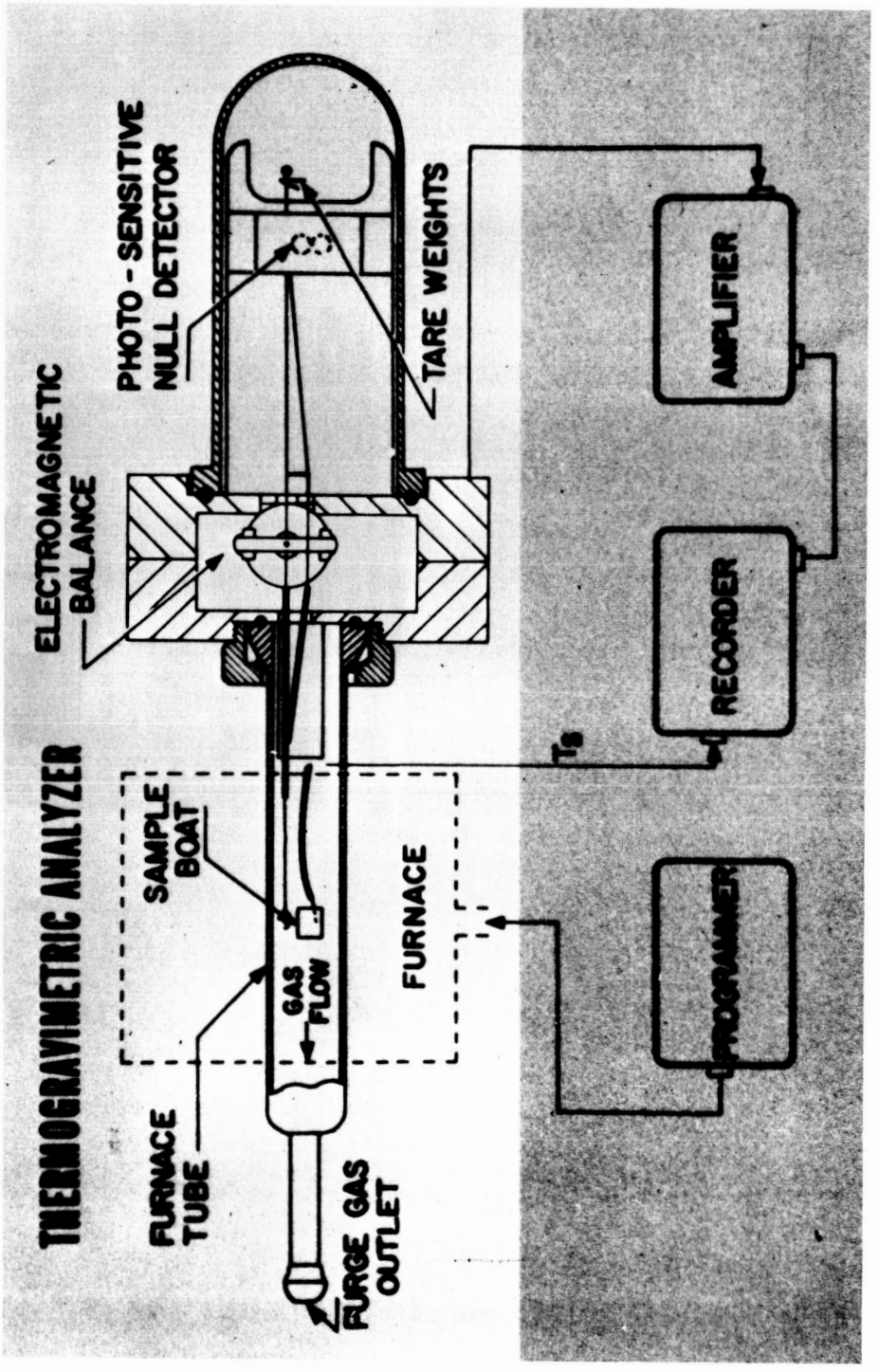
THERMOGRAVIMETRIC ANALYZER
ELECTROMAGNETIC BALANCE
PHOTO-SENSITIVE NULL DETECTOR
TARE WEIGHTS
SAMPLE BOAT
FURNACE TUBE
GAS FLOW
FURNACE
PURGE GAS OUTLET
T_S
AMPLIFIER
RECORDER
PROGRAMMER

Fig. 3-3

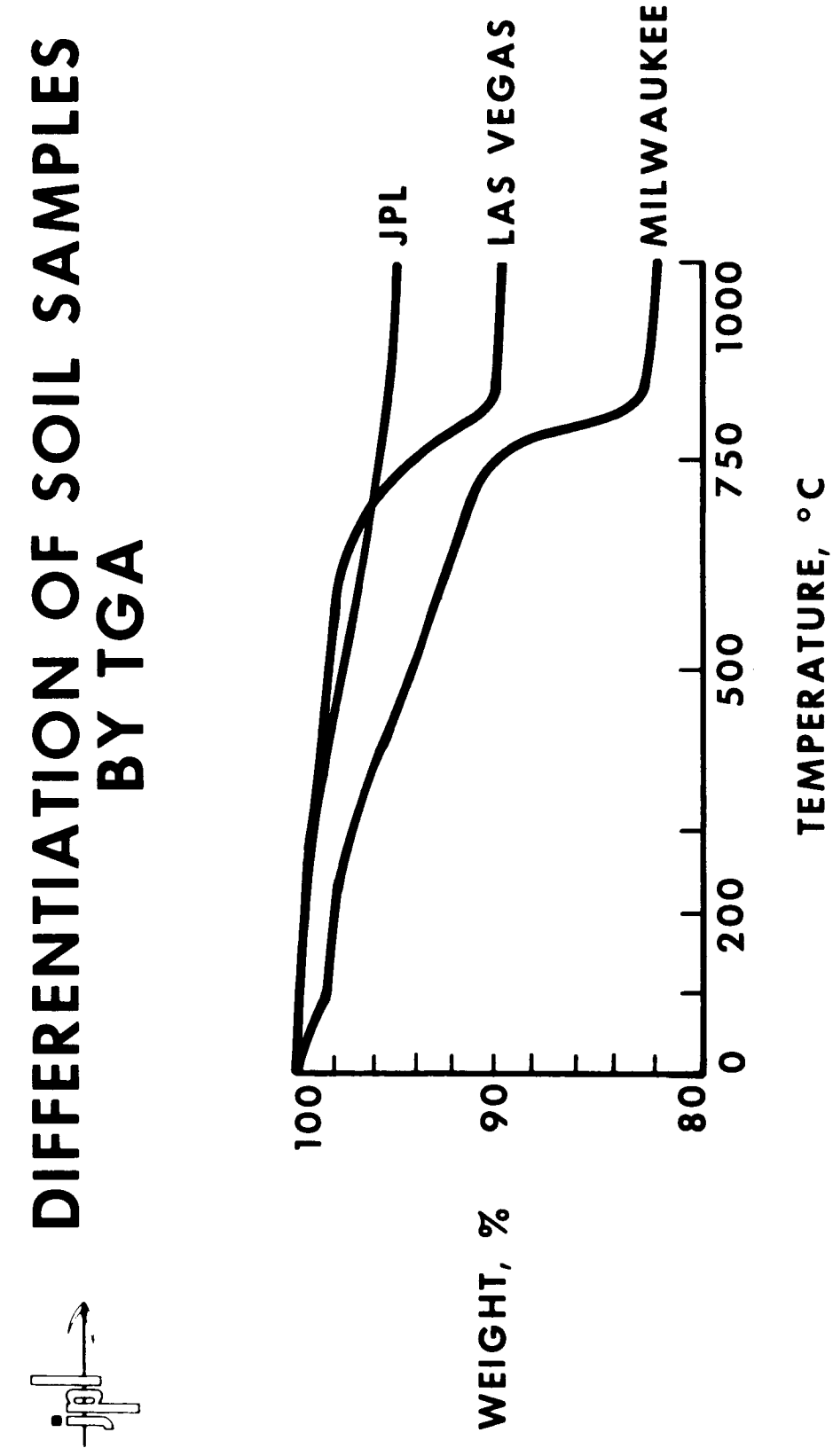
DIFFERENTIATION OF SOIL SAMPLES BY TGA
JPL
LAS VEGAS
MILWAUKEE
100
90
80
0
200
500
750
1000
WEIGHT, %
TEMPERATURE, °C

Fig. 3-4

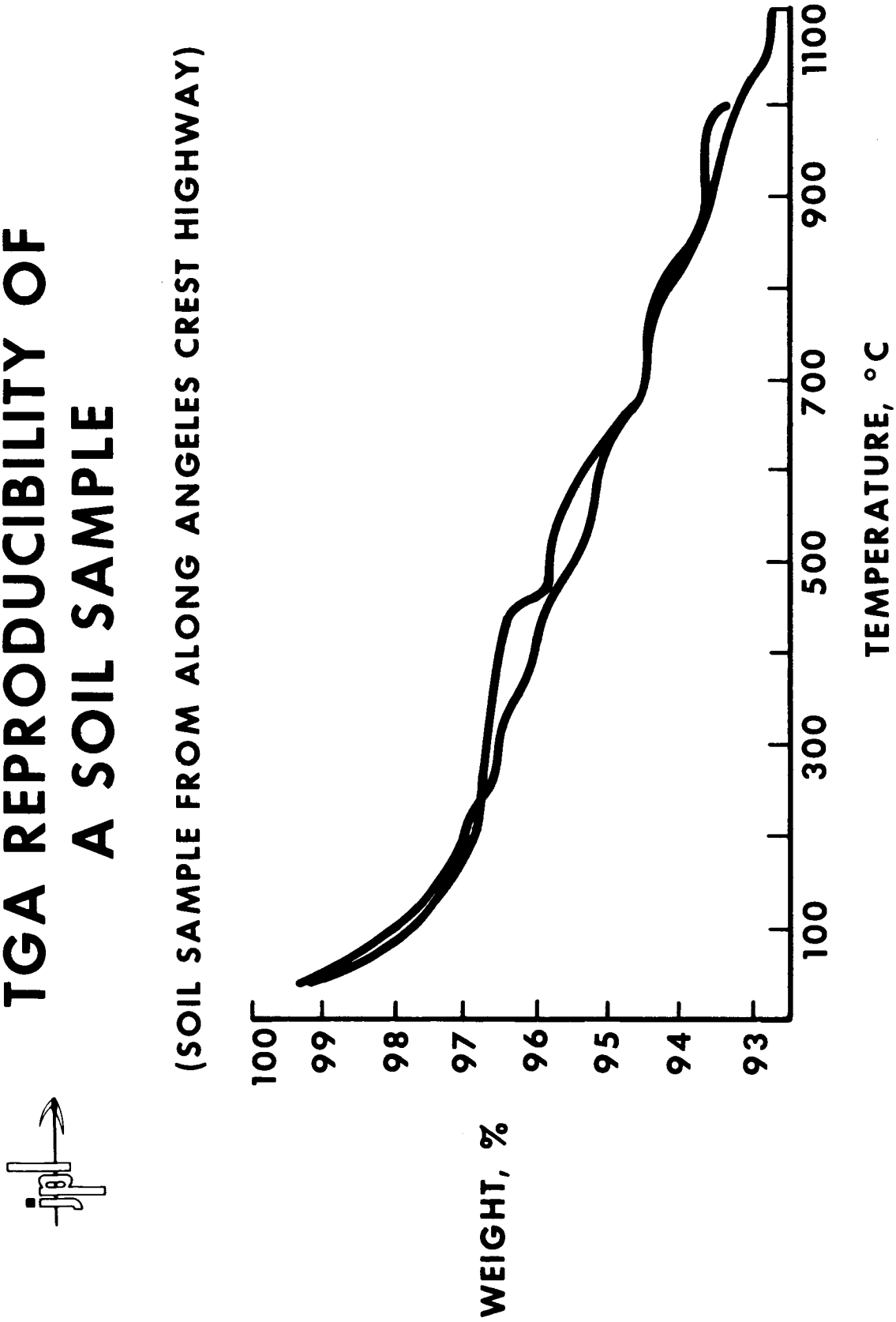
TGA REPRODUCIBILITY OF A SOIL SAMPLE
(SOIL SAMPLE FROM ALONG ANGELES CREST HIGHWAY)
WEIGHT, %
100
99
98
97
96
95
94
93
100
300
500
700
900
1100
TEMPERATURE, °C

Fig. 3-5

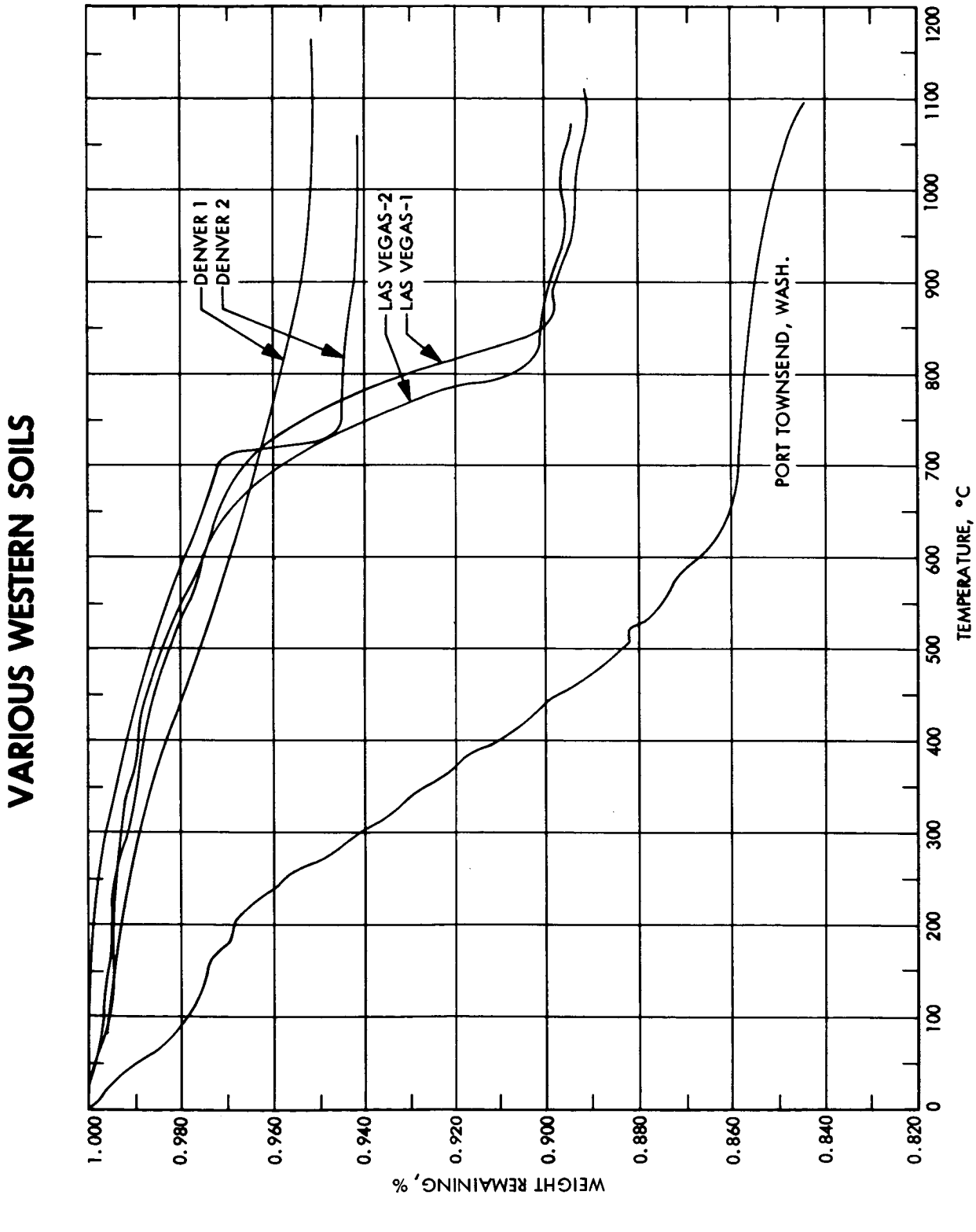
VARIOUS WESTERN SOILS
DENVER 1
DENVER 2
LAS VEGAS-2
LAS VEGAS-1
PORT TOWNSEND, WASH.
WEIGHT REMAINING, %
1.000
0.980
0.960
0.940
0.920
0.900
0.880
0.860
0.840
0.820
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
TEMPERATURE, °C

Fig. 3-6

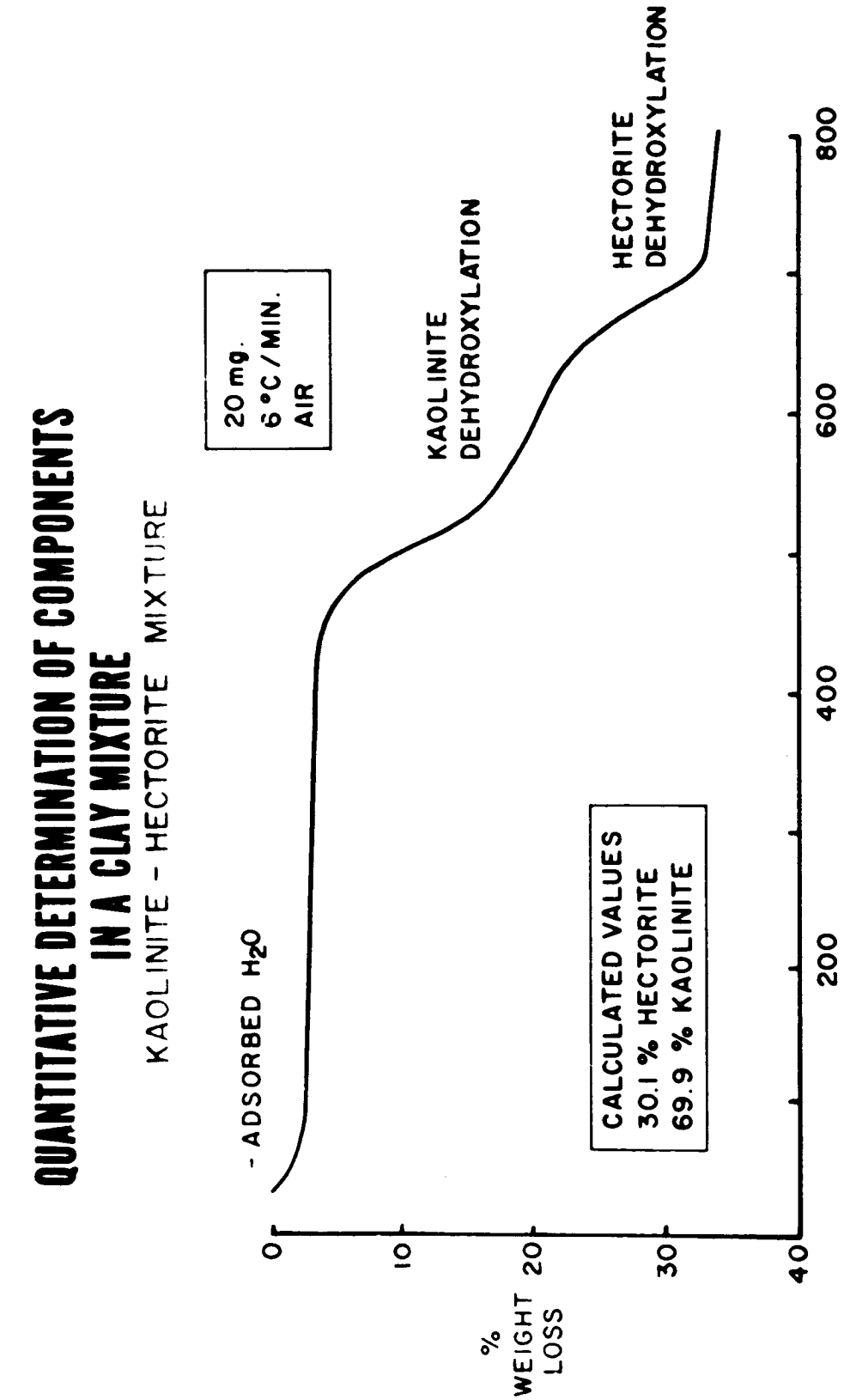
QUANTITATIVE DETERMINATION OF COMPONENTS IN A CLAY MIXTURE
KAOLINITE - HECTORITE MIXTURE
20 mg.
6 °C / MIN.
AIR
- ADSORBED H2O
KAOLINITE DEHYDROXYLATION
HECTORITE DEHYDROXYLATION
CALCULATED VALUES
30.1 % HECTORITE
69.9 % KAOLINITE
% WEIGHT LOSS
0
10
20
30
40
200
400
600
800
TEMPERATURE, °C

Fig. 3-7

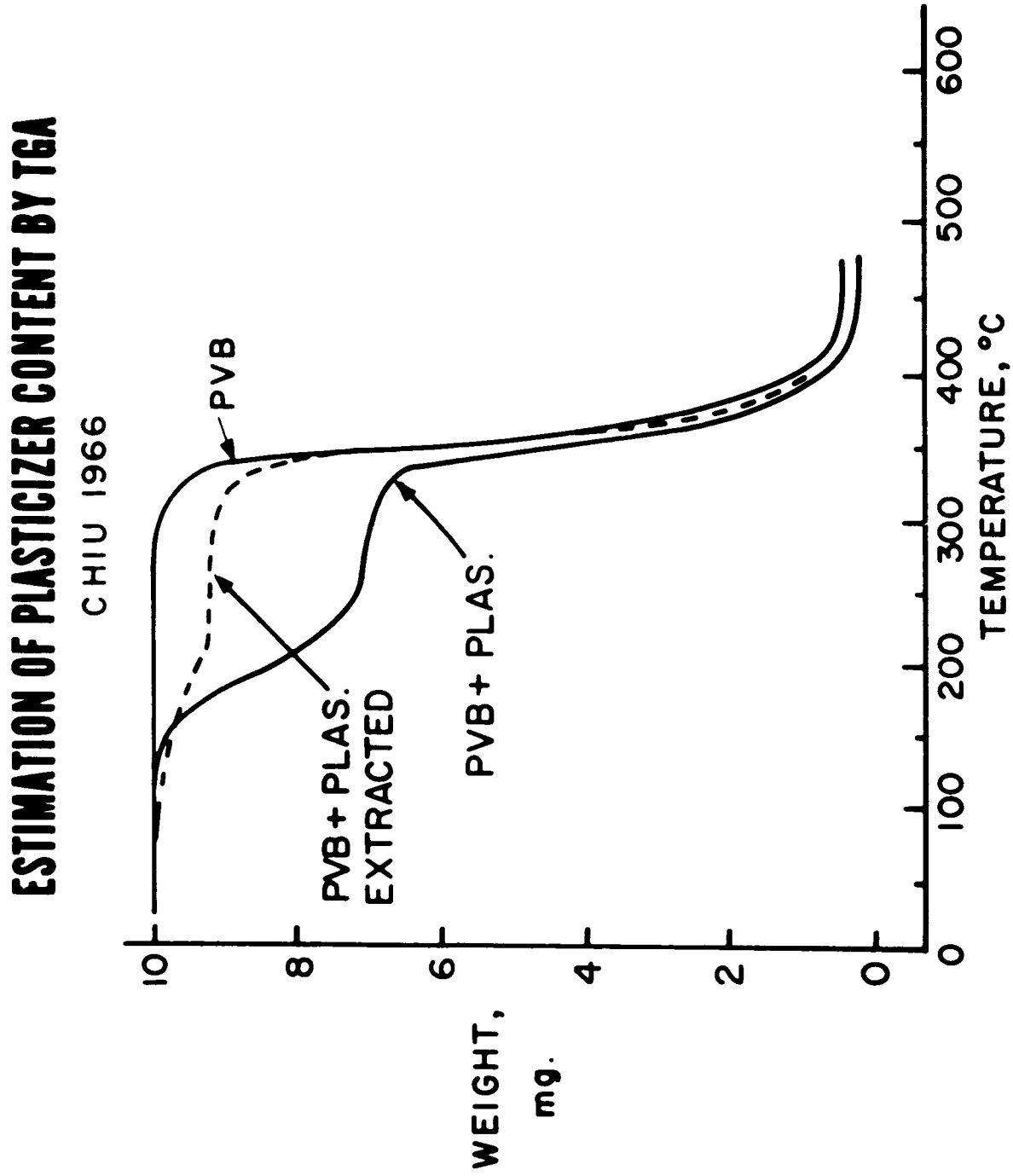
ESTIMATION OF PLASTICIZER CONTENT BY TGA
CHIU 1966
PVB
PVB+ PLAS. EXTRACTED
PVB+ PLAS.
WEIGHT, mg.
10
8
6
4
2
0
0
100
200
300
400
500
600
TEMPERATURE, °C

Fig. 3-8

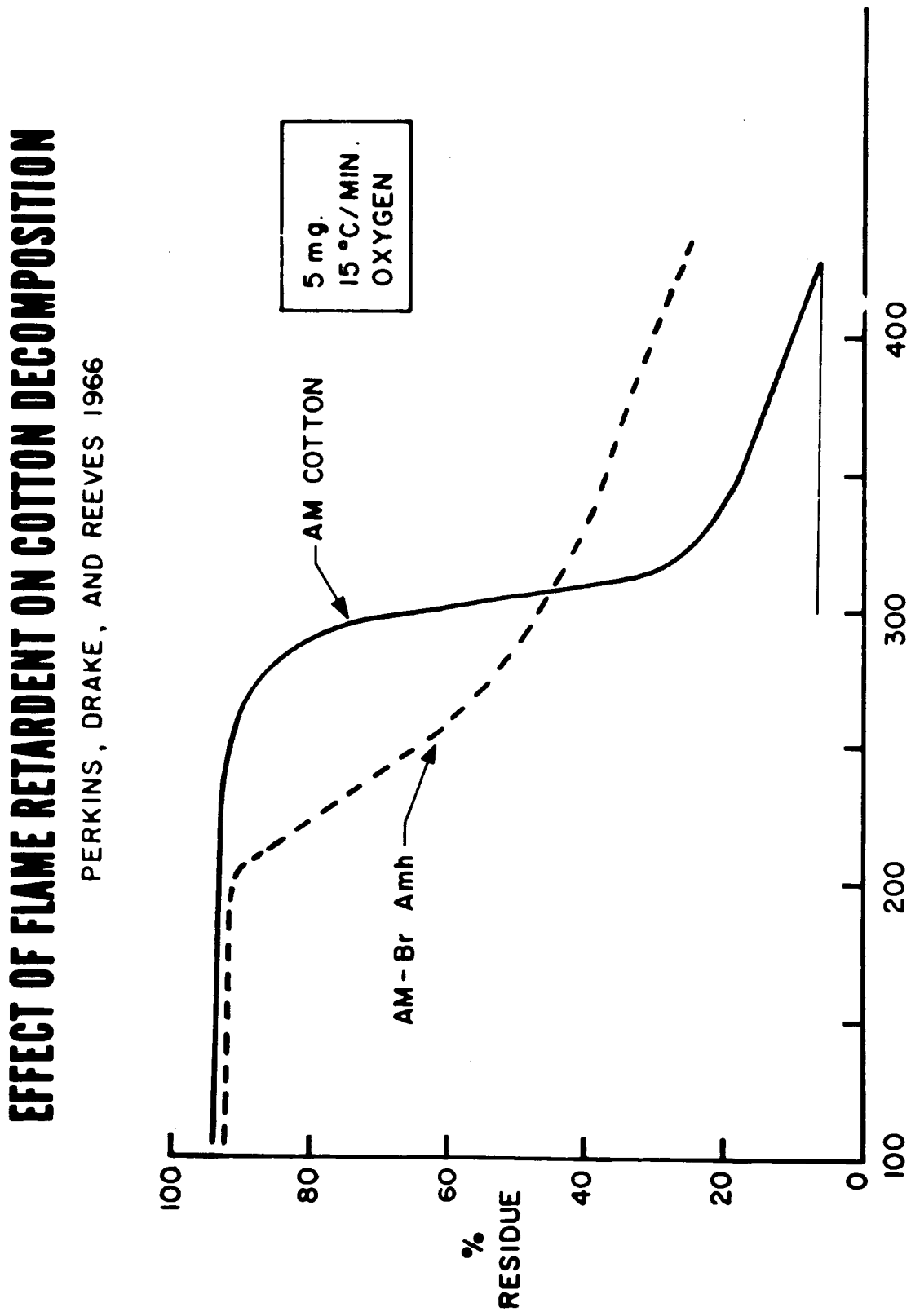
EFFECT OF FLAME RETARDENT ON COTTON DECOMPOSITION
PERKINS, DRAKE, AND REEVES 1966
5 mg.
15 °C/MIN.
OXYGEN
AM COTTON
AM-Br Amh
% RESIDUE
100
80
60
40
20
0
100
200
300
400
TEMPERATURE, °C

Fig. 3-9

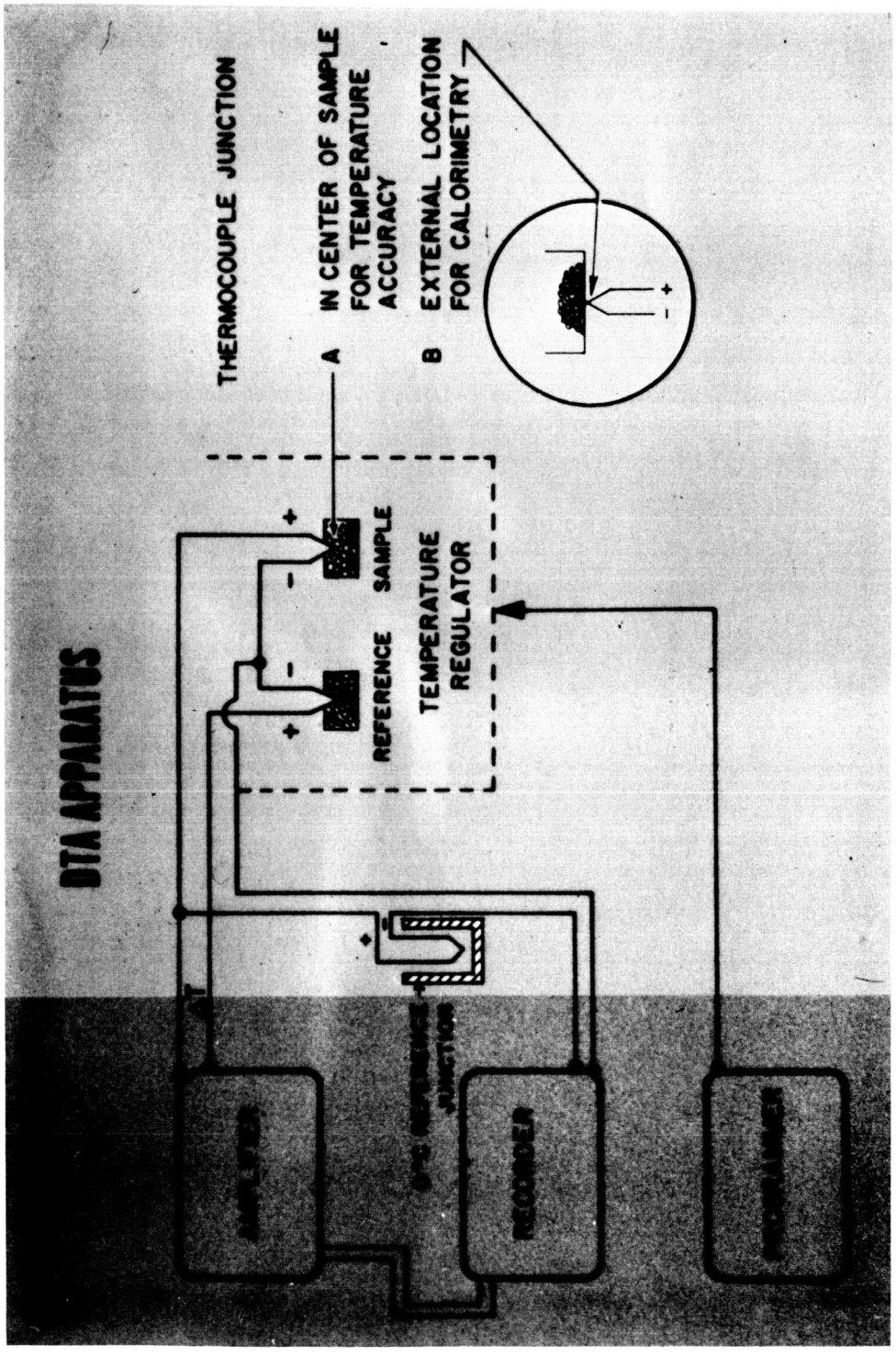
DTA APPARATUS
THERMOCOUPLE JUNCTION
A IN CENTER OF SAMPLE FOR TEMPERATURE ACCURACY
B EXTERNAL LOCATION FOR CALORIMETRY
SAMPLE
REFERENCE
TEMPERATURE REGULATOR
AMPLIFIER
RECORDER
COMPUTER

Fig. 3-10

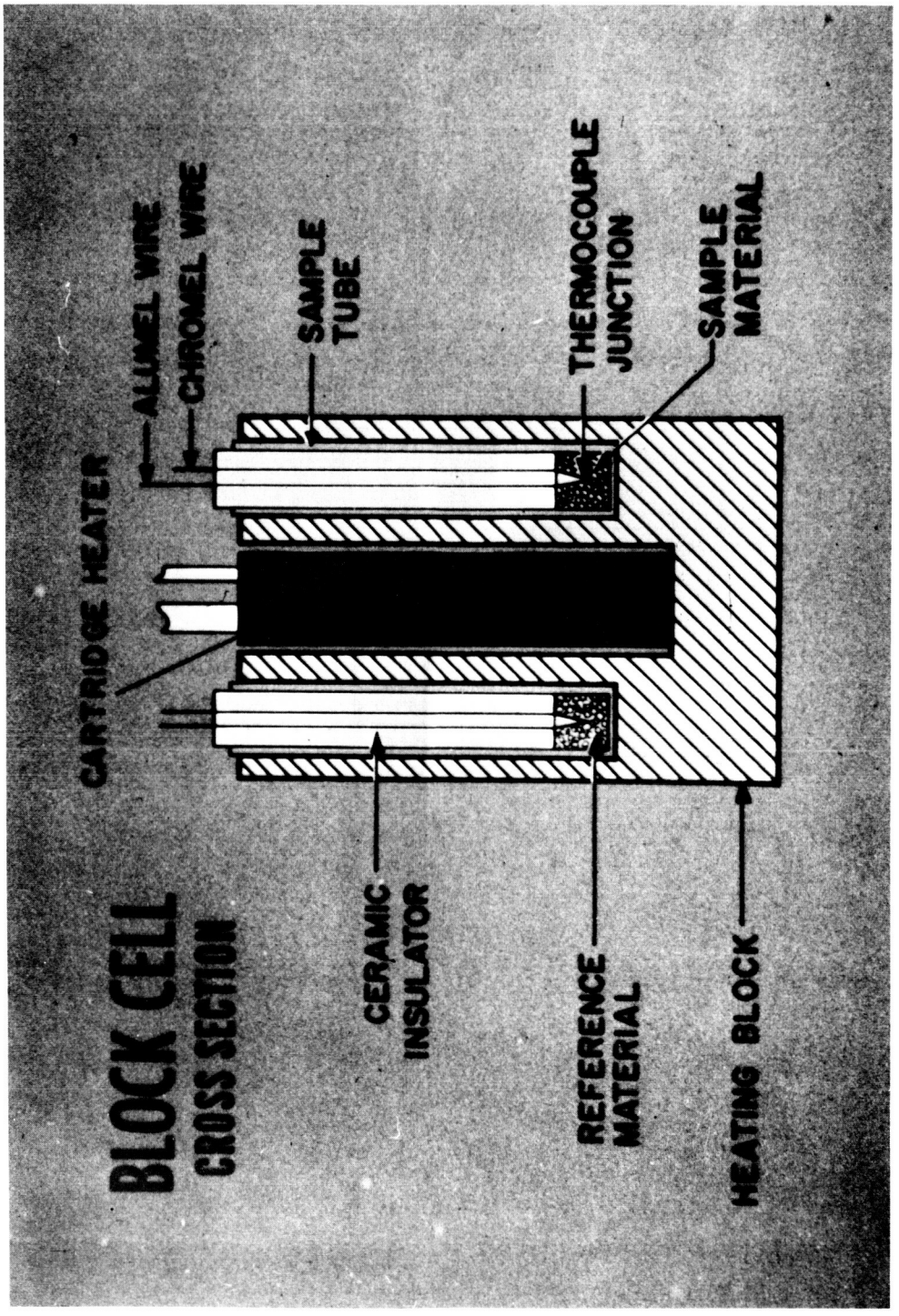
BLOCK CELL
CROSS SECTION
CARTRIDGE HEATER
ALUMEL WIRE
CHROMEL WIRE
SAMPLE TUBE
THERMOCOUPLE JUNCTION
SAMPLE MATERIAL
CERAMIC INSULATOR
REFERENCE MATERIAL
HEATING BLOCK

Fig. 3-11

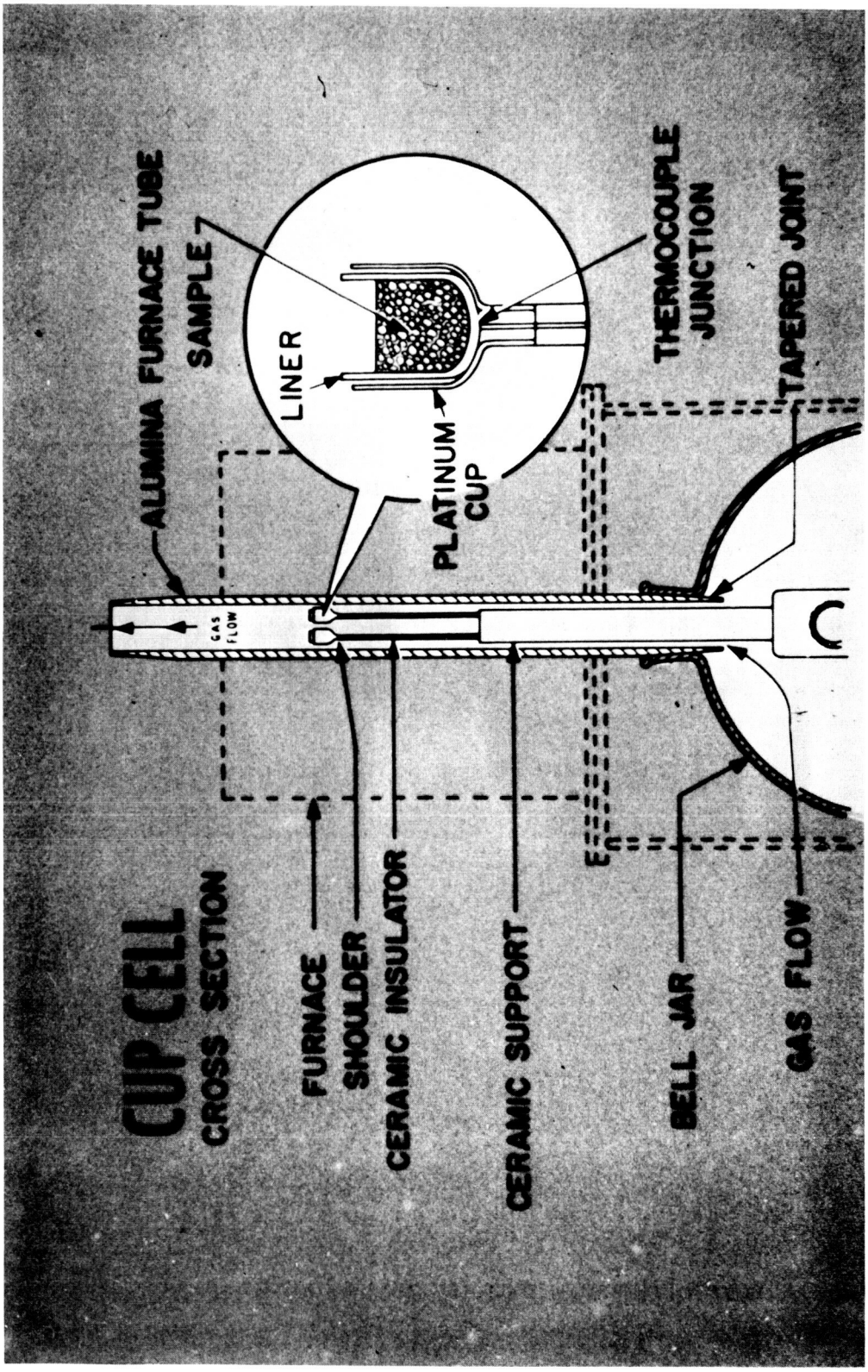
CUP CELL
CROSS SECTION
ALUMINA FURNACE TUBE
SAMPLE
LINER
PLATINUM CUP
THERMOCOUPLE JUNCTION
TAPERED JOINT
GAS FLOW
FURNACE
SHOULDER
CERAMIC INSULATOR
CERAMIC SUPPORT
BELL JAR
GAS FLOW

Fig. 3-12

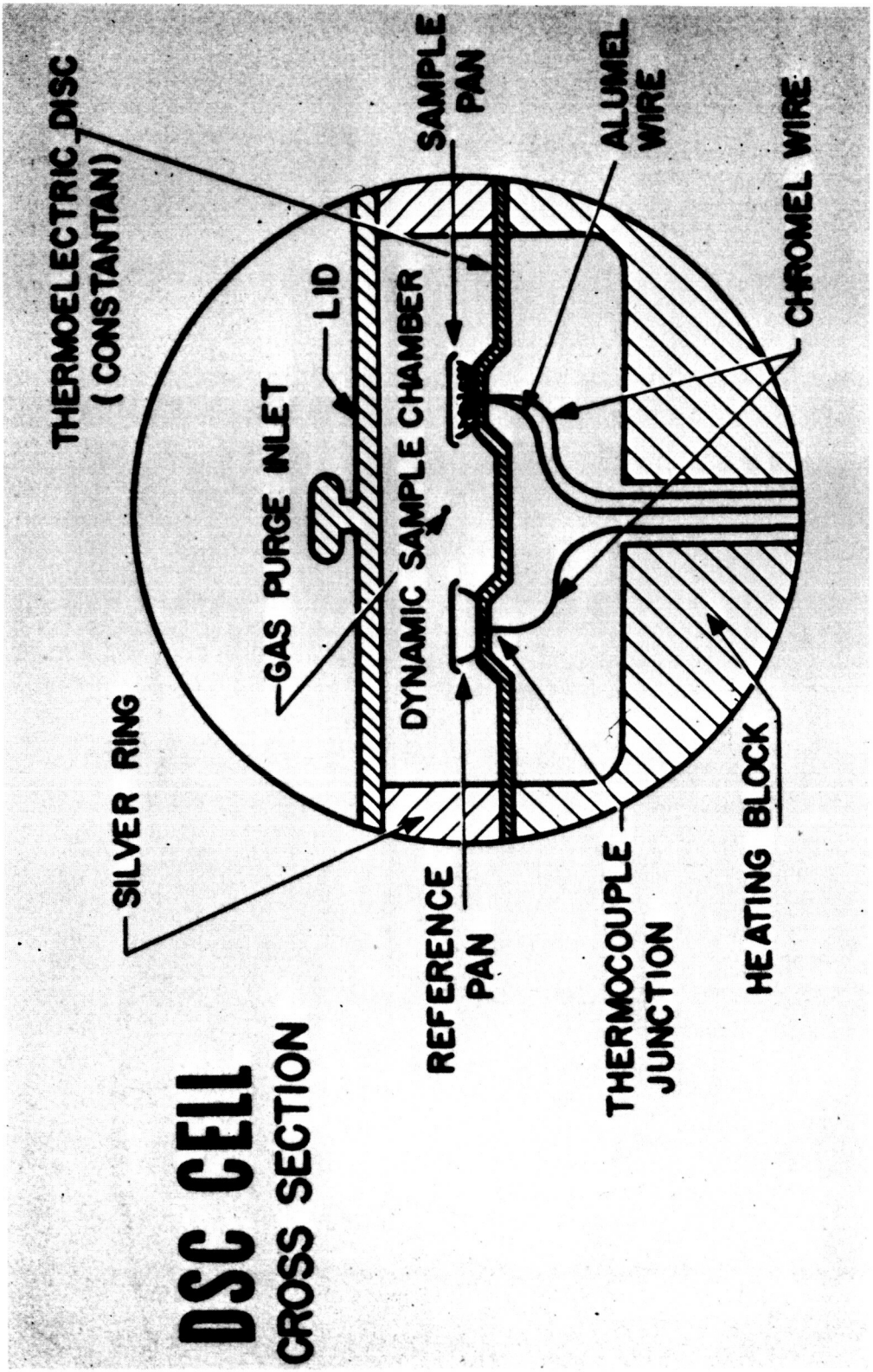
DSC CELL
CROSS SECTION
SILVER RING
THERMOELECTRIC DISC
(CONSTANTAN)
GAS PURGE INLET
LID
DYNAMIC SAMPLE CHAMBER
SAMPLE PAN
ALUMEL WIRE
CHROMEL WIRE
REFERENCE PAN
THERMOCOUPLE JUNCTION
HEATING BLOCK

Fig. 3-13

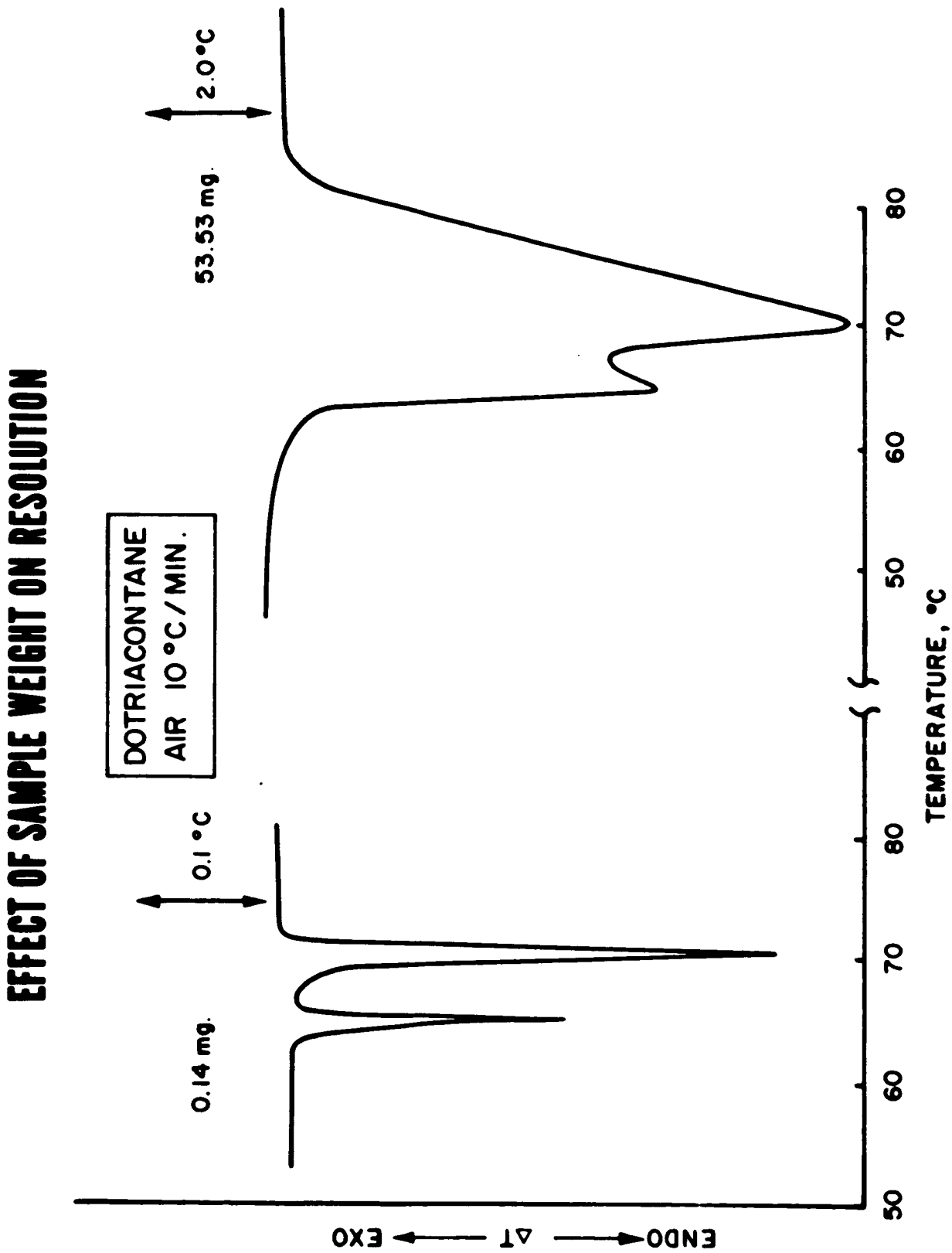
EFFECT OF SAMPLE WEIGHT ON RESOLUTION
DOTRIACONTANE
AIR 10 °C / MIN.
0.14 mg.
0.1 °C
53.53 mg.
2.0°C
ENDO ← ΔT → EXO
TEMPERATURE, °C
50
60
70
80
50
60
70
80

Fig. 3-14

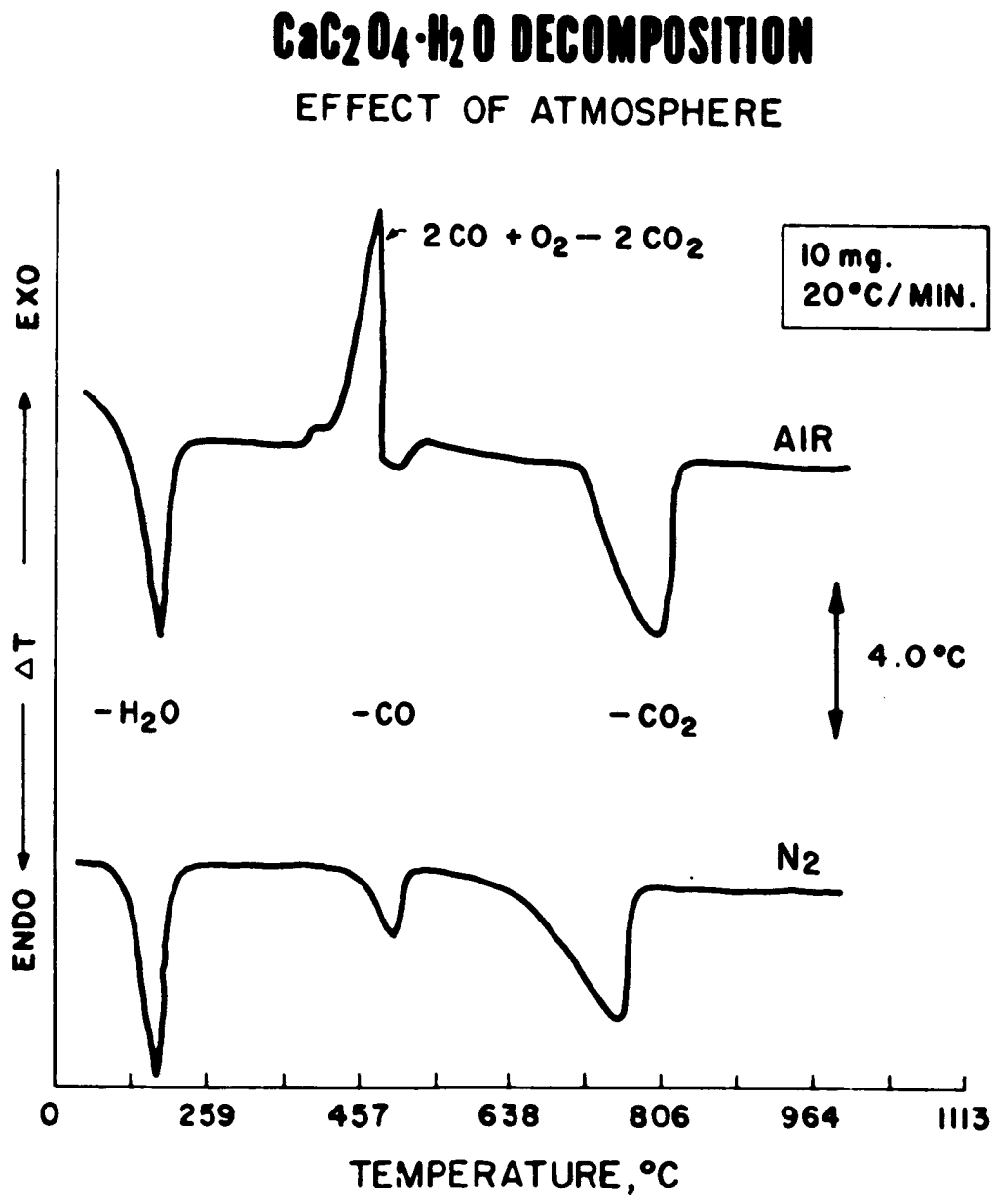
$CaC_2O_4 \cdot H_2O$ DECOMPOSITION
EFFECT OF ATMOSPHERE
$2CO + O_2 - 2CO_2$
10 mg.
20°C/MIN.
AIR
N_2
EXO
ENDO
ΔT
4.0°C
$-H_2O$
$-CO$
$-CO_2$
0
259
457
638
806
964
1113
TEMPERATURE, °C

Fig. 3-15

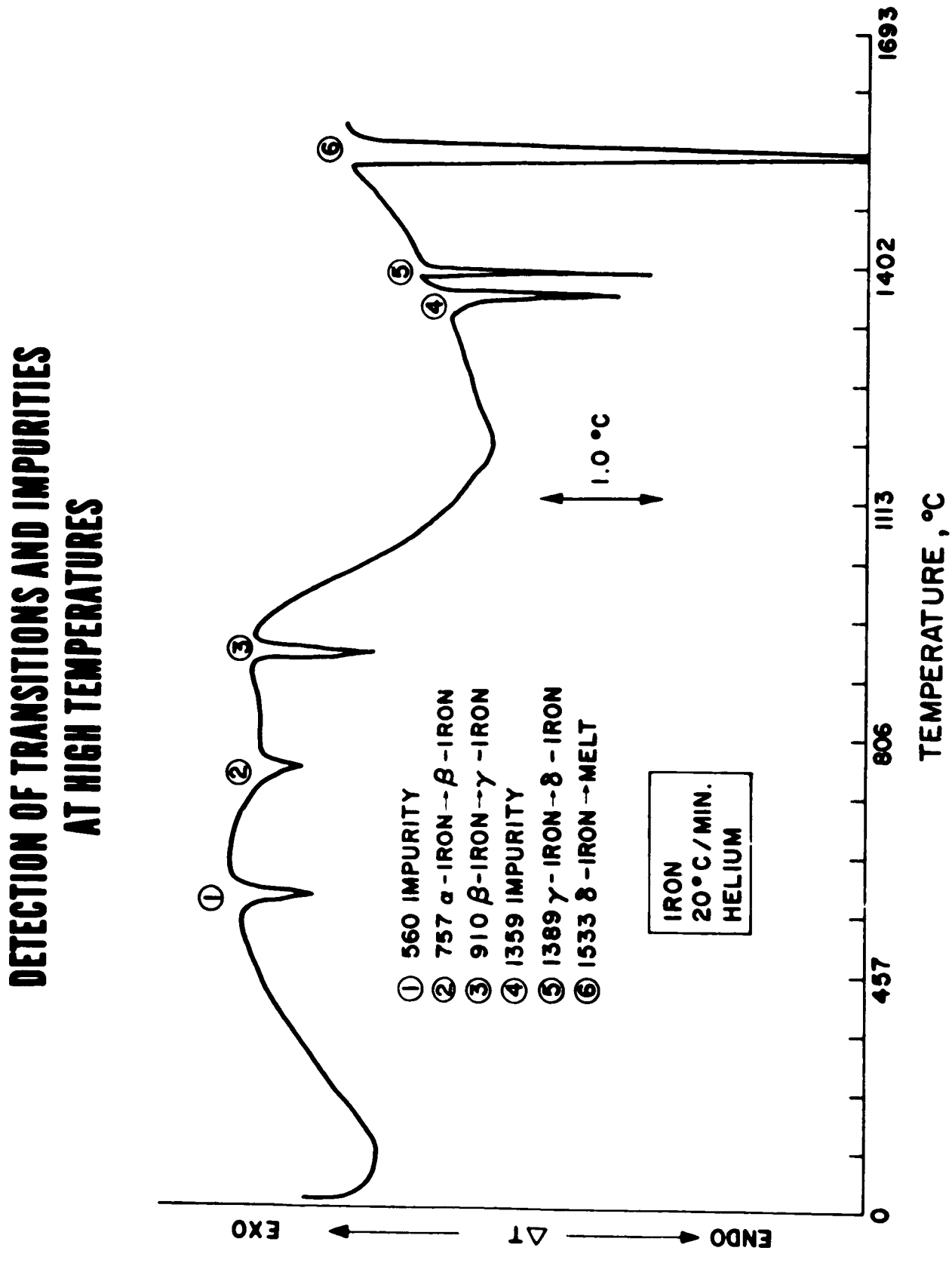
DETECTION OF TRANSITIONS AND IMPURITIES AT HIGH TEMPERATURES
EXO
ΔT
ENDO
0
457
806
1113
1402
1693
TEMPERATURE, °C
1.0 °C
IRON
20°C/MIN.
HELIUM
① 560 IMPURITY
② 757 α-IRON→β-IRON
③ 910 β-IRON→γ-IRON
④ 1359 IMPURITY
⑤ 1389 γ-IRON→δ-IRON
⑥ 1533 δ-IRON→MELT

Fig. 3-16

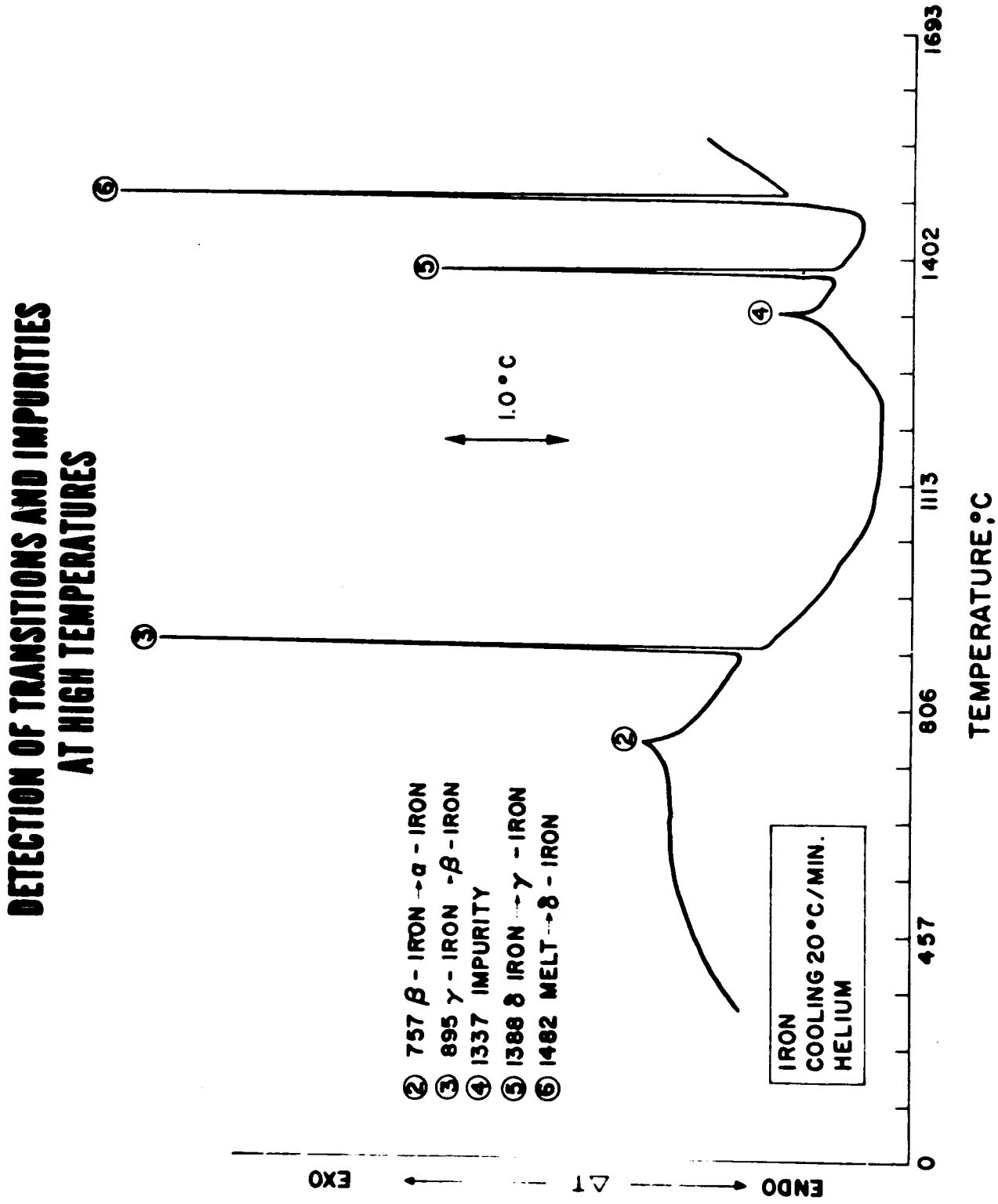
DETECTION OF TRANSITIONS AND IMPURITIES AT HIGH TEMPERATURES
1.0°C
② 757 β - IRON → α - IRON
③ 895 γ - IRON → β - IRON
④ 1337 IMPURITY
⑤ 1388 δ IRON → γ - IRON
⑥ 1482 MELT → δ - IRON
IRON
COOLING 20°C/MIN.
HELIUM
ENDO
ΔT
EXO
0
457
806
1113
1402
1693
TEMPERATURE, °C

Fig. 3-17

DETECTION OF TRANSITIONS AND IMPURITIES AT HIGH TEMPERATURES

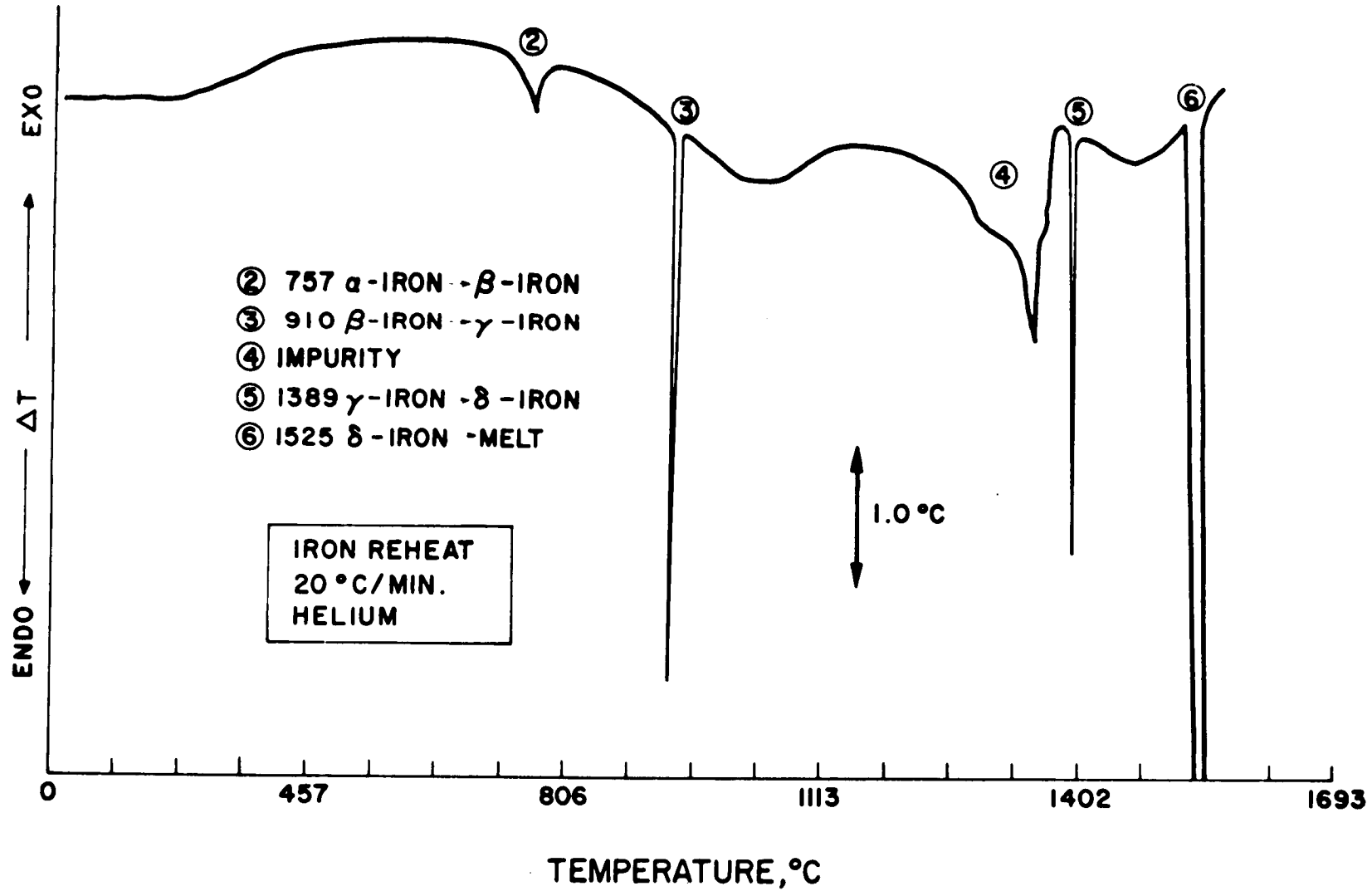

Fig. 3-18

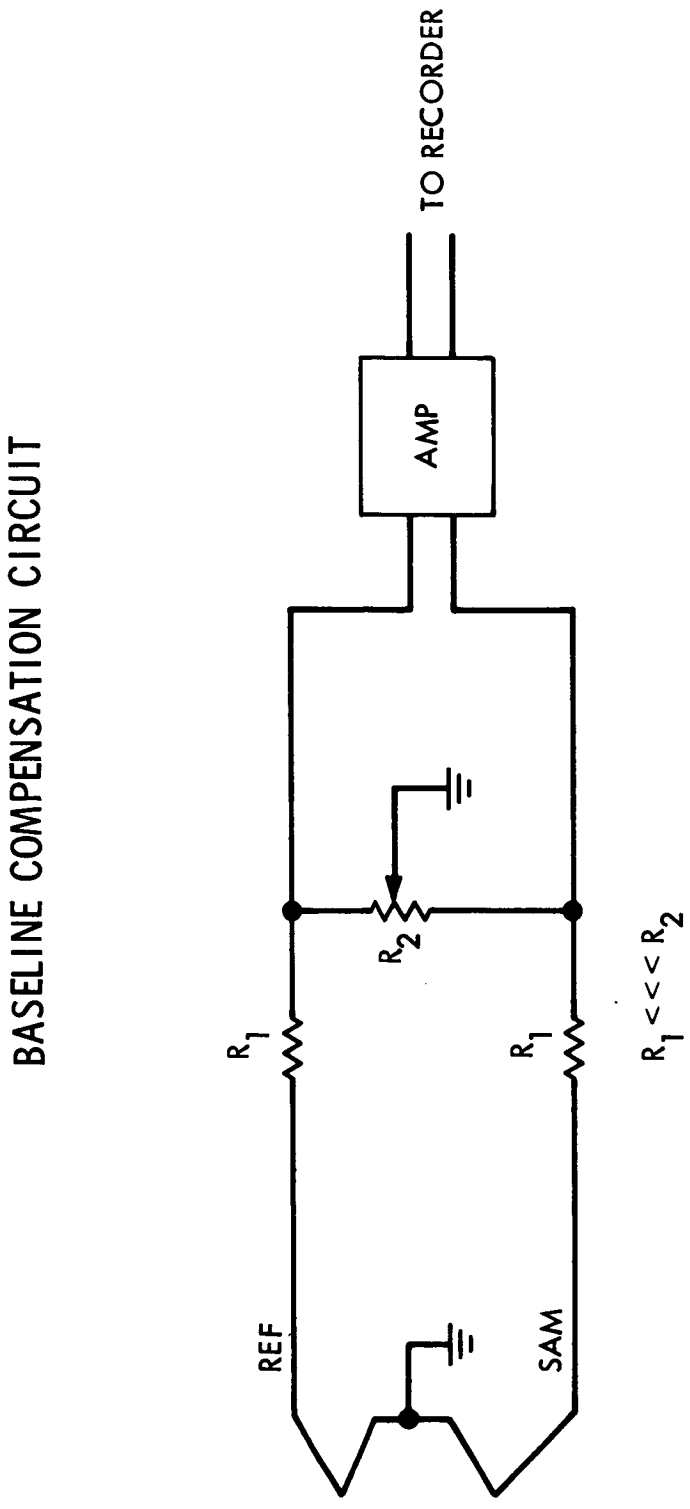
BASELINE COMPENSATION CIRCUIT
TO RECORDER
AMP
R_2
R_1
R_1
$R_1 <<< R_2$
REF
SAM
R_D - UNIFORM CLOSELY CONTROLLED OPTIMUM VALUE

Fig. 3-19

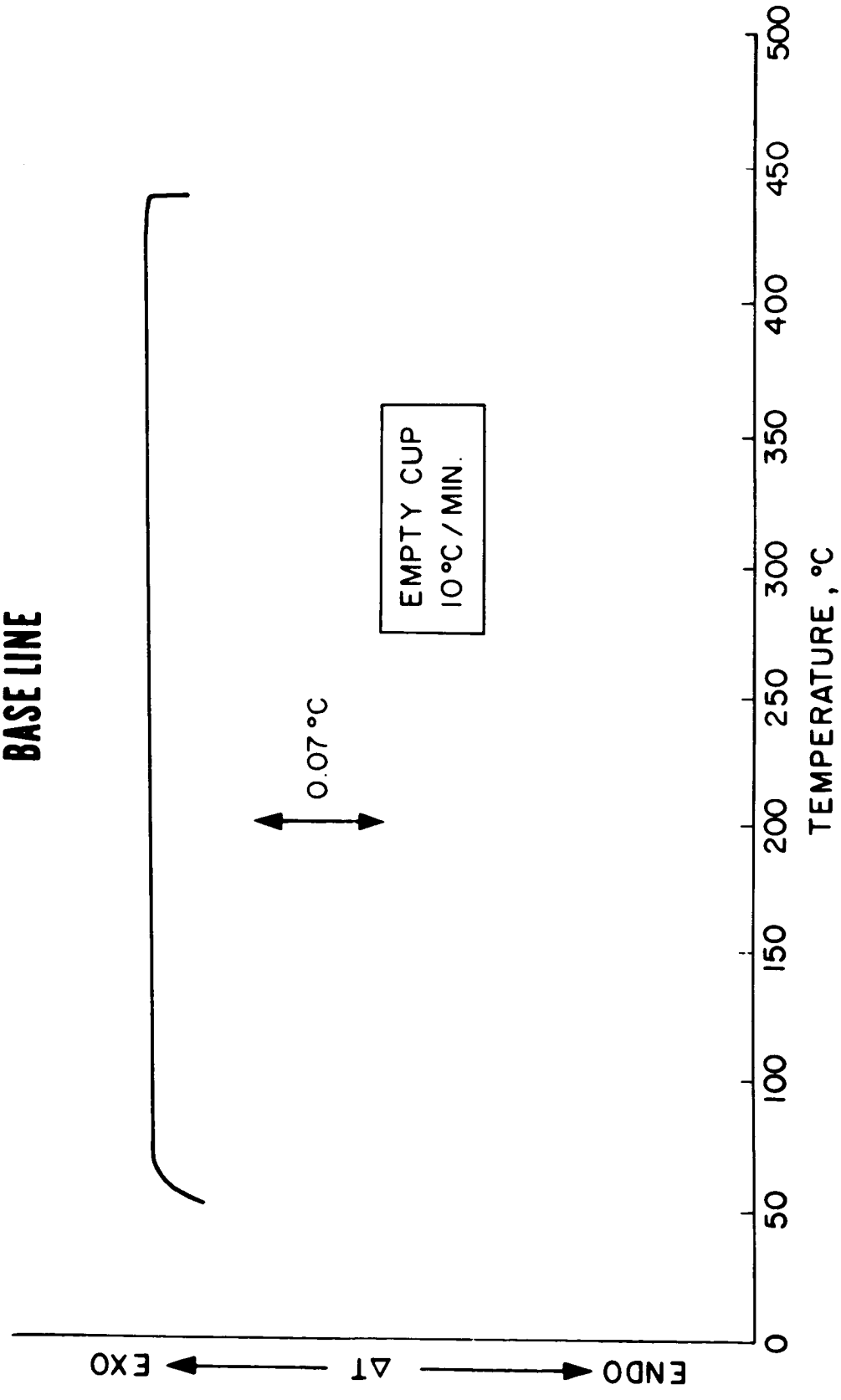
BASE LINE
0.07 °C
EMPTY CUP
10 °C / MIN.
0
50
100
150
200
250
300
350
400
450
500
TEMPERATURE, °C
ENDO
ΔT
EXO

Fig. 3-20

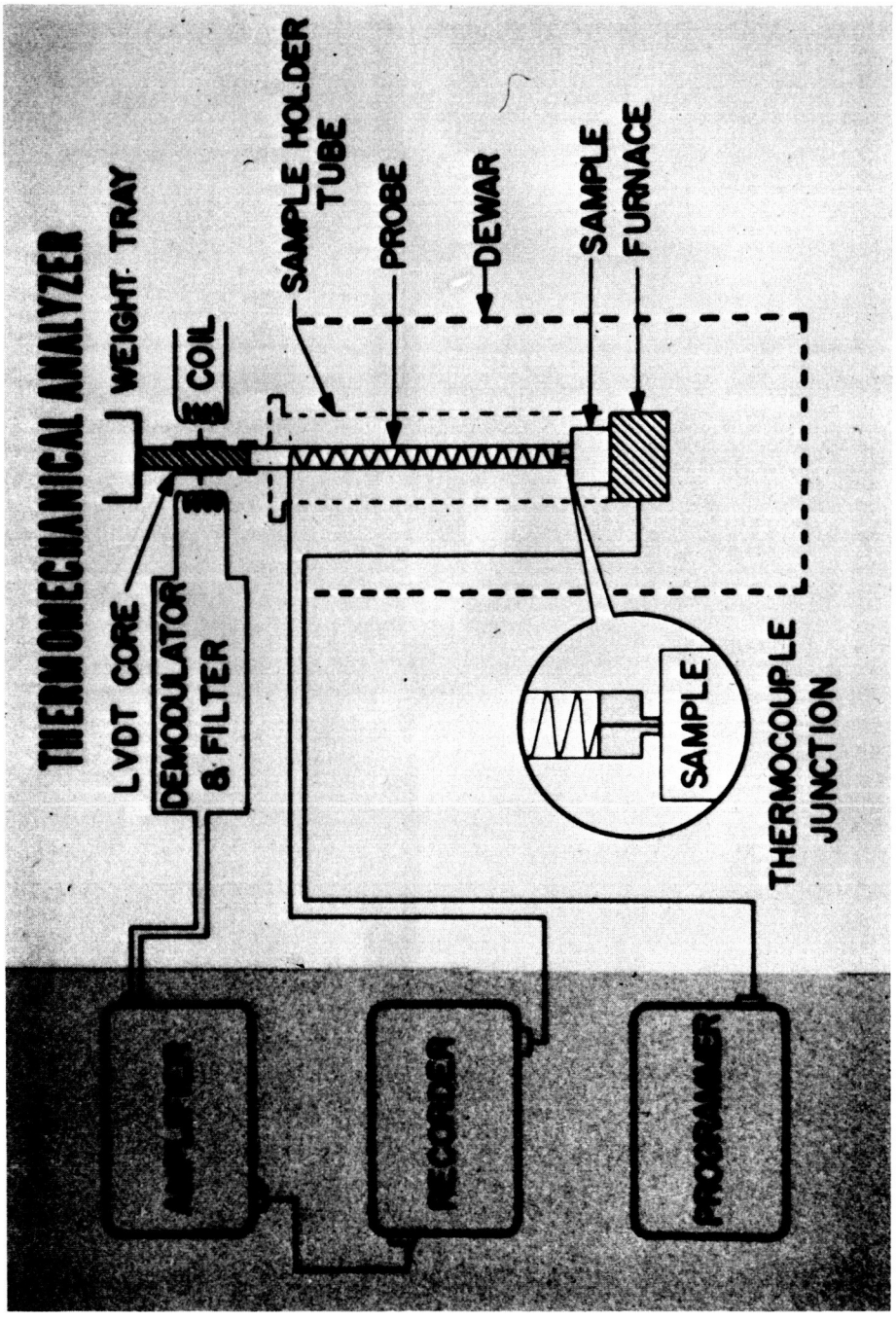
THERMOMECHANICAL ANALYZER
WEIGHT TRAY
COIL
SAMPLE HOLDER TUBE
PROBE
DEWAR
SAMPLE FURNACE
LVDT CORE
DEMODULATOR & FILTER
SAMPLE
THERMOCOUPLE JUNCTION
RECORDER
PROGRAMMER

Fig. 3-21

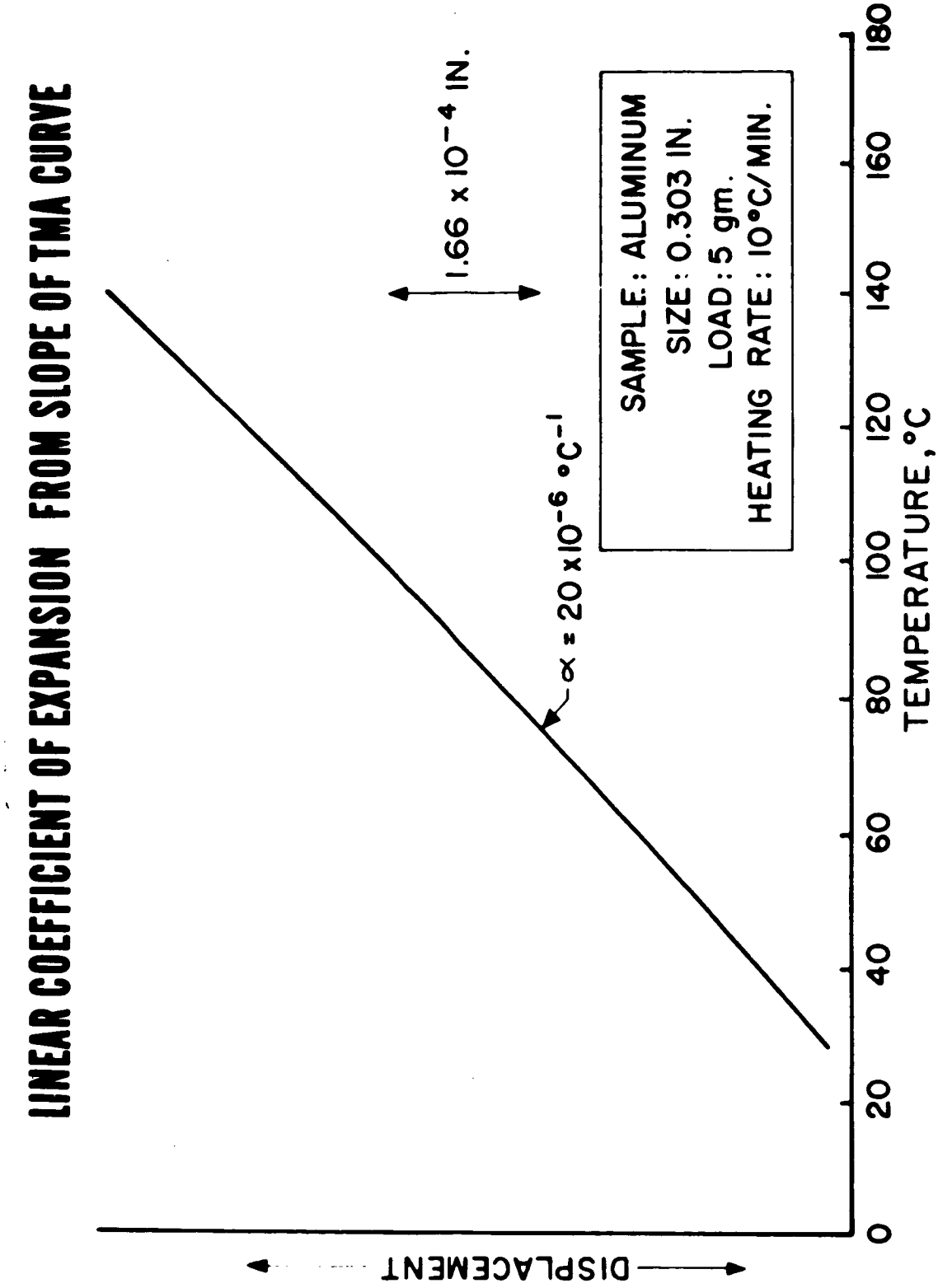
LINEAR COEFFICIENT OF EXPANSION FROM SLOPE OF TMA CURVE
DISPLACEMENT
1.66 x 10⁻⁴ IN.
α = 20 x 10⁻⁶ °C⁻¹
SAMPLE: ALUMINUM
SIZE: 0.303 IN.
LOAD: 5 gm.
HEATING RATE: 10°C/MIN.
0
20
40
60
80
100
120
140
160
180
TEMPERATURE, °C

Fig. 3-22

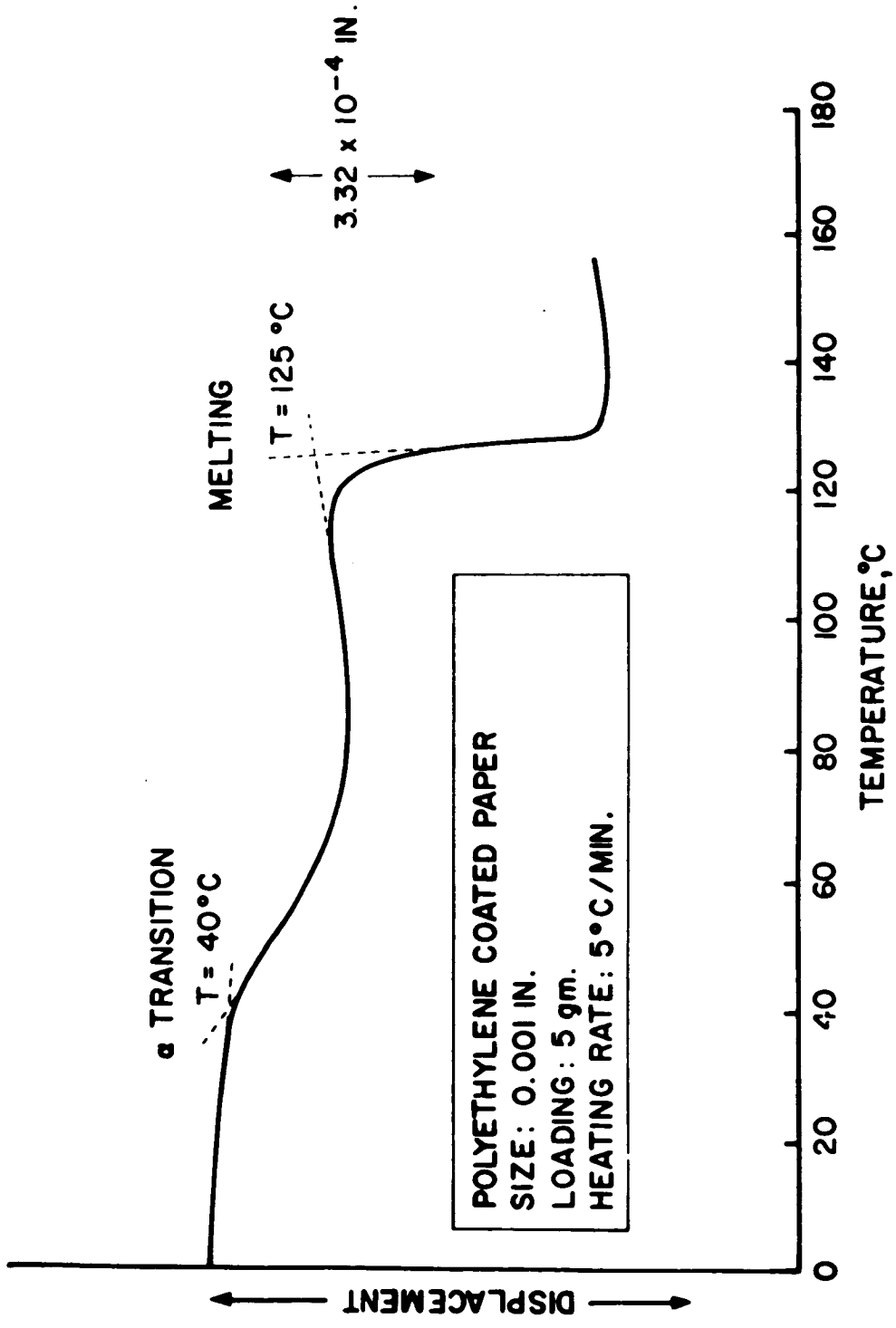
DETECTION OF TRANSITIONS IN THIN COATINGS BY PENETRATION
α TRANSITION
T = 40°C
MELTING
T = 125 °C
3.32 x 10⁻⁴ IN.
POLYETHYLENE COATED PAPER
SIZE: 0.001 IN.
LOADING: 5 gm.
HEATING RATE: 5°C/MIN.
DISPLACEMENT
0
20
40
60
80
100
120
140
160
180
TEMPERATURE,°C

Fig. 3-23

CURE OF COATINGS BY TMA

(HOLSWORTH,R)

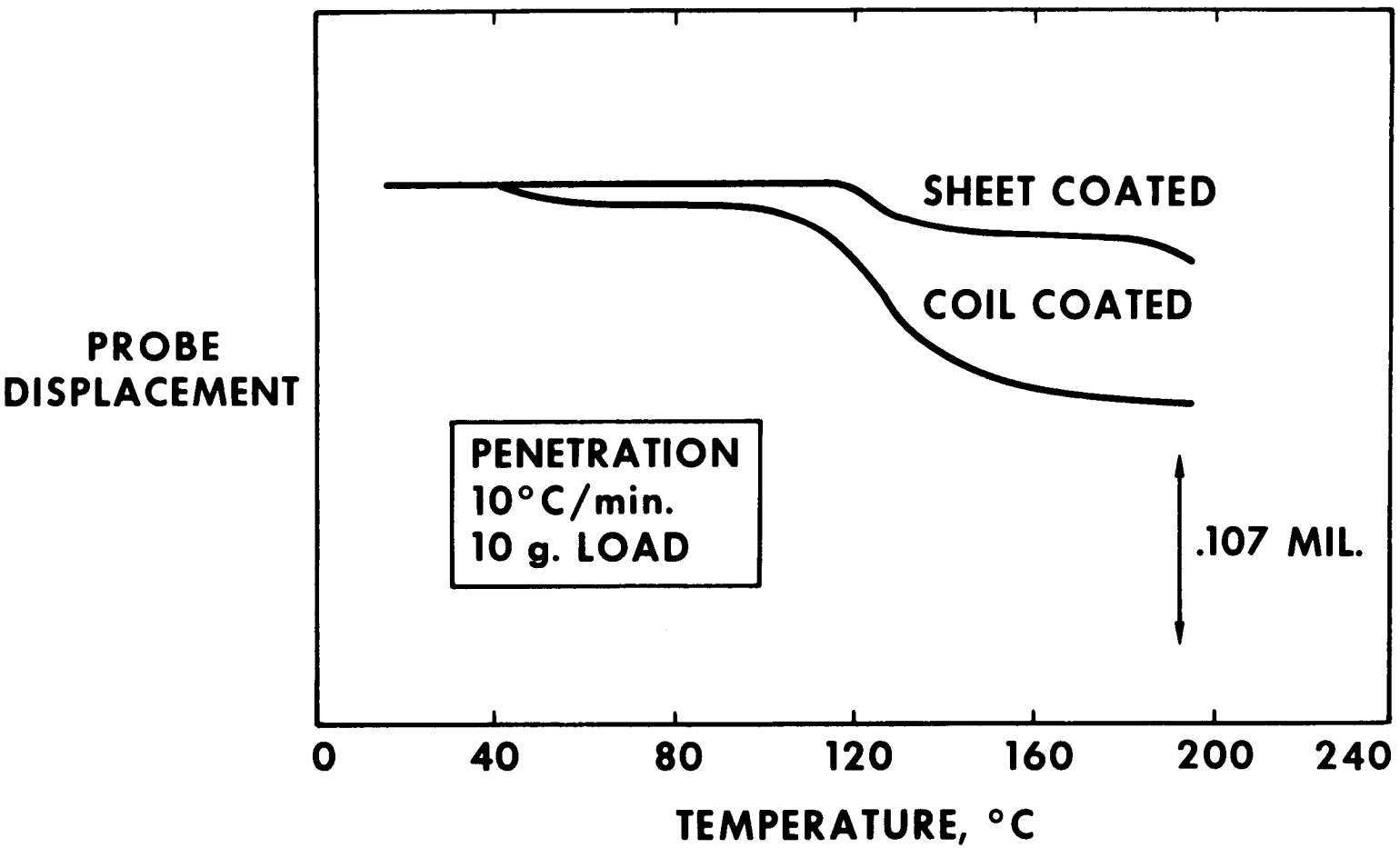

Fig. 3-24

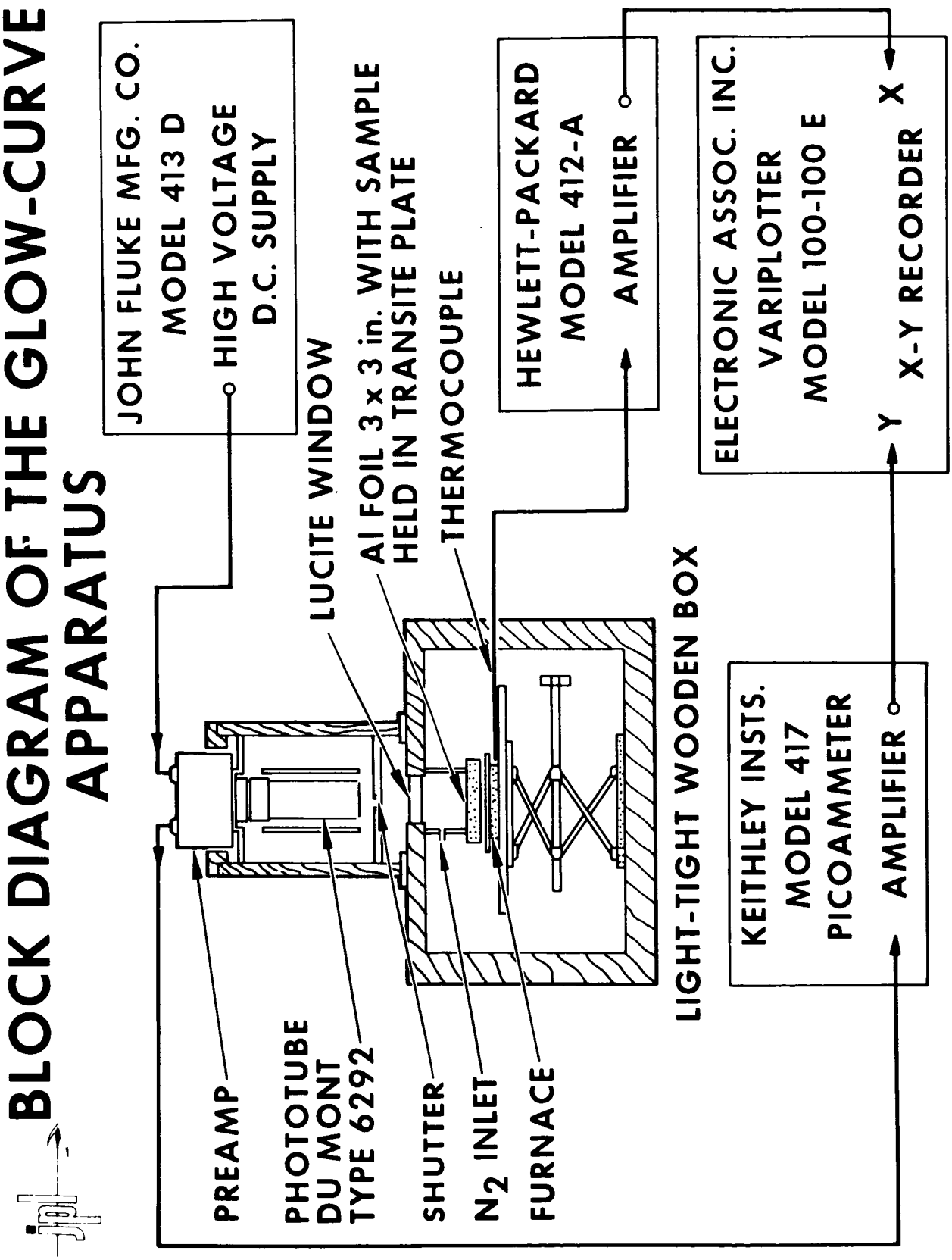
BLOCK DIAGRAM OF THE GLOW-CURVE APPARATUS
JOHN FLUKE MFG. CO.
MODEL 413 D
HIGH VOLTAGE
D.C. SUPPLY
LUCITE WINDOW
Al FOIL 3 x 3 in. WITH SAMPLE
HELD IN TRANSITE PLATE
THERMOCOUPLE
HEWLETT-PACKARD
MODEL 412-A
AMPLIFIER
ELECTRONIC ASSOC. INC.
VARIPLOTTER
MODEL 100-100 E
X
X-Y RECORDER
Y
PREAMP
PHOTOTUBE
DU MONT
TYPE 6292
SHUTTER
N_2 INLET
FURNACE
LIGHT-TIGHT WOODEN BOX
KEITHLEY INSTS.
MODEL 417
PICOAMMETER
AMPLIFIER

Fig. 3-25

GLOW CURVE OF A THERMOLUMINESCENT CRYSTAL MEASURED SIMULTANEOUSLY WITH A THERMAL BLEACHING CURVE WHICH SHOWS THE CHANGE IN ABSORBANCE AT 3500 Å AS THE CRYSTAL IS HEATED

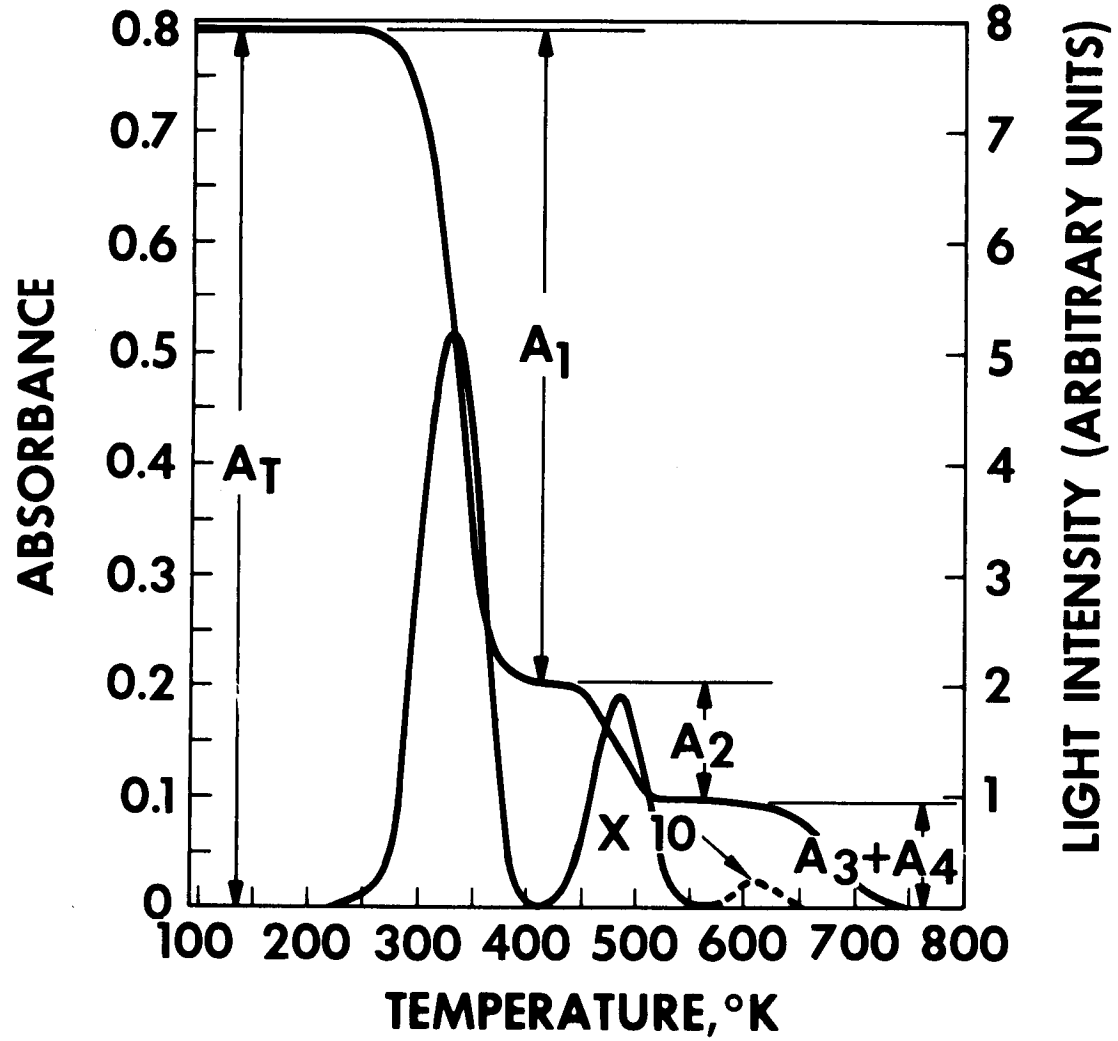

Fig. 3-26

A REVIEW OF THE CURRENT STATUS OF MASS SPECTROMETRY, CHROMATOGRAPHY, AND PYROLYSIS AS TOOLS FOR THE DETECTION AND IDENTIFICATION OF COMPLEX ORGANIC COMPOUNDS

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Jet Propulsion Laboratory, California Institute of Technology
Pasadena, California

I. INTRODUCTION

This presentation reviews the current status of mass spectrometry, gas chromatography, thin layer and micro dry column chromatography, and pyrolysis as tools for the identification of complex organic compounds.

II. MASS SPECTROMETRY

A. HISTORY

The basic principle of mass spectrometry (MS) was demonstrated by W. Wien in 1898 and by J. J. Thompson in 1912. The first instruments were developed by A. J. Dempster in 1918 and by F. W. Aston in 1919. In 1943, the first analytical applications in quantitative precision analysis of very complex mixtures of hydrocarbons were made by H. W. Washburn, et al. After the first commercial mass spectrometers appeared, the technique of mass spectrometry has developed rapidly through the

measurement of stable isotopes and the development of isotope ratio mass spectrometers by A. O. Nier, et al., in 1947, to high resolution mass spectrometry in organic structural analysis by Beynon and Biemann during the mid to late 1950s. Today, MS is a widely used analytical technique for the identification and structural characterization of organic compounds.

B. GENERAL THEORY

In mass spectrometry, the mass spectrum is a recording of RELATIVE ABUNDANCE vs MASS. In one type of recording, one mass is focused after the other on a collector slit. In the other technique, all masses are focused in a plane with simultaneous recording of all masses.

C. CHARACTERISTICS, PHYSICAL AND FUNCTIONAL

1. Resolution:

   Typical single-focusing magnetic deflection systems have a resolving power up to 1/10,000 while double focusing analyzers have a resolving power up to 1/1,000,000.

2. Repeatability:

   The MS has excellent repeatability. Quantitative reproducibility can be better than 0.1%.

3. Specificity:

   MS has a high degree of specificity.

4. Quantitation:

   Quantitative accuracy is better than 0.1% under optimum conditions.

5. Sensitivity:

   The mass spectrometer has high sensitivity up to 10^{-14} g/sec. It provides the largest amount of information per microgram of any analytical technique.

6. Sample Preparation and Size:

   In MS, little sample preparation is required for the majority of the samples. For a compound to be analyzed, it must be able to be volatilized at a reasonable temperature in a high vacuum. Samples of very low volatility have to be derivatized, if possible, to form more volatile species, or preliminary fractionation may be required by means of GC, extraction, or other means. The lower limit of the sample size is usually

below the level that can be manipulated conveniently (from a fraction of a nanogram to a few micrograms). The upper limit is set by the pressure of the ion source and thus by the volatility of the sample.

D. CHARACTERISTICS, OPERATIONAL

1. Time for Analyses:

   MS analysis time ranges from a few seconds in the GC mode to 30 min or more for a tenacious sample in the probe mode.

2. Training:

   Training requirements for the MS vary from a reasonably skilled conscientious technician for routine analyses to an academically highly trained and very experienced person for the structural analysis of complex compounds.

3. Maintenance:

   MS maintenance requirements are somewhat higher than the average laboratory instrument. Annual maintenance cost, including supplies and salary, is usually in the same order as the initial purchase price. Contract maintenance is available and may be cheaper than hiring your own technician.

E. COSTS

MS equipment costs more than most laboratory instruments, from a $25,000 minimum to a maximum of $350,000. However, because of the tremendous amount of samples that can be processed and information that can be gained, the cost per sample is still very low.

F. INSTRUMENTAL PARAMETERS

In this section, a fully equipped MS laboratory is described including the two main types of mass revolving systems, the single-focusing magnetic deflection (see Fig. 4-1) and the double focusing magnetic deflection (see Fig. 4-2), as well as other mass spectrometers. Ion sources and ion collectors with sensitivity up to 10^{-14} g/sec or counting of single ions are discussed. Figure 4-3 shows an electron bombardment ion source. Sample introduction through reservoir and molecular leak, direct evaporation, or the GC inlet are explained. Data recording and analysis are also covered.

The methods of analyzing low resolution data and high resolution data are explained. It is noted that low resolution data can be carried out manually or by machine, with the latter obviously more efficient. High resolution data is employed for compound identification only when low resolution reference spectra do not exist.

G. APPLICATIONS TO ORGANIC CHEMISTRY

For MS analysis, a compound must be able to be volatilized at a reasonable temperature in a high vacuum. In this context, volatilization can be vaporization without decomposition, in which case a spectrum of the intact molecule is obtained, or vaporization by thermal degradation, taking place either in the high vacuum of the source chamber or near atmospheric pressure in the "pyrolysis" inlet of the GC inlet system.

In the field of organic chemistry, MS is used for gas analysis, by the oil industry, by general chemical service laboratories to analyze mixtures of volatile compounds, in the analysis of the atmosphere of the earth and planets, and in trace analysis. MS is used by the pharmaceutical, oil, chemistry, and aerospace industries for qualitative analyses of more than 50 compound types and many biochemical classes (Figs. 4-4 and 4-5).

Some art museums are now using MS analysis for authentication. Recently, MS analyses have been presented and accepted as evidence in court in a few criminal cases.

III. GAS CHROMATOGRAPHY

A. HISTORY

The earliest work in the field of chromatography were papers by Runge (1850) and Tswett (1906). However, gas chromatography (GC) as such was first mentioned in Martin and Synge's paper on Elution Chromatography in 1941. The technique was demonstrated experimentally for the first time by James and Martin in 1952. By 1955, almost every analytical laboratory had a gas chromatograph. Today, GC is one of the most universal analytical techniques. It is especially useful as a tool for separating complex mixtures and for quantitation of the separated fractions. Figure 4-6 shows the essential components of a gas chromatograph. A simple schematic is shown in Fig. 4-7

B. GENERAL THEORY

Elution chromatography is based upon the principles of solution, adsorption, and/or partitioning. There are several modes of operation: fluid-solid chromatography where the sample is transported by an inert fluid through a bed of active adsorbent, and gas-liquid chromatography where the sample is carried by an inert gas through a bed of solid support coated with a liquid partitioning agent. The latter mode primarily is discussed in this presentation (see Fig. 4-8).

C. CHARACTERISTICS, PHYSICAL AND FUNCTIONAL

1. Repeatability:

   GC has a quantitative repeatability of 0.1% under optimum conditions.

2. Quantitation:

   The primary field of GC is quantitative analysis of mixtures of even extreme complexity. The best reported accuracy, using internal standards and edification, is 0.1%.

3. Sensitivity:

   Sensitivity is high (10^{-13} g/sec).

4. Sample Preparation and Size:

   Only a small sample and a minimal amount of preparation is required. The only major step is to volatilize derivatives of those materials not otherwise suitable for GC analysis.

D. CHARACTERISTICS, OPERATIONAL

1. Time for Analyses:

   GC, used with a computerized data acquisition and processing system, can be incredibly fast.

2. Training:

   Highly trained operators are not required for GC.

3. Maintenance:

One of the advantages of GC is its low operation and maintenance cost.

E. COST

A simple chromatograph and recorder may be purchased for as low as $2,000, while an elaborate multi-chromatograph/computerized data system combination may run more than $50,000.

F. APPLICATIONS TO ORGANIC CHEMISTRY

The range of GC applications to organic chemistry is very similar to that of MS. If a sample can be volatilized by simple vaporization or by pyrolysis, it can be analyzed by GC. Mixtures of as many as several hundred components have been analyzed successfully.

IV. GAS CHROMATOGRAPHY/MASS SPECTROMETRY

A. HISTORY

The first reports on combined gas chromatography/mass spectrometry (GC/MS) were made in 1957 by Holmes and Morrell, Gohlke, and Johns, et al.

B. GENERAL THEORY

In GC/MS, the effluent gas of the chromatograph is passed into the ion source of the mass spectrometer. Spectra are taken either continuously or whenever a peak emerges. In the latter case, a peak detector is required. Somewhere between the chromatograph's inlet system and the MS's analyzer, the pressure of the carrier gas has to be reduced. This is accomplished either by a high speed differential pumping system or a molecular separator.

GC/MS is used in most of the fields where either is used by itself.

C. SPECIAL REQUIREMENTS FOR A GC/MS INSTRUMENT

1. GC Requirements:

   a. The elution rate of the GC peaks must be matched to the maximum possible scan rate of the mass spectrometer.

   b. The column system should be selected in such a way that a minimum of carrier gas is used while still remaining near the optimum on the HETP curve.

   c. The stationary phases must be limited to those with extremely low bleed rates and their maximum operating temperatures must be restricted in order to avoid high background and/or fouling of the MS.

2. The Interface Requirements:

   The basic interface requirement is to remove a maximum amount of carrier gas with a minimum loss of sample. The carrier gas must also be inert with the sample.

3. MS Requirements:

   a. Scan speed must be fast enough to scan a reasonably fast GC peak without excessive distortion of the spectrum due to changes of concentration profile (see Fig. 4-9).

   b. Sensitivity of the MS should be at least 10^{-12} g ms/sec.

   c. A differentially pumped ion source with pumping speeds in excess of 100 lit/sec is desirable.

   d. The data system must be capable of handling a relatively large number of spectra in a short period of time.

D. APPLICATIONS

GC/MS is a very valuable analytical tool when one knows or suspects that a sample is impure, as in the analysis of foods, flavors, and odors (see Fig. 4-10) and of fatty acids in biological materials and foodstuffs (Fig. 4-11). It is also used in the determination of petroleum products (see Fig. 4-12). In these cases of impure compounds, the GC/MS provides better analyses than other techniques because it gives cleaner spectra.

GC/MS is used in geo-and cosmo-chemistry, in atmospheric analysis, in the space program to analyze meteoric and lunar samples, and in criminalistics. Figure 4-13 lists some applications of GC/MS to biochemical and health problems, health hazards, and law enforcement problems.

The real point of using GC/MS is that identification will be absolute.

V. THIN LAYER AND MICRO DRY COLUMN CHROMATOGRAPHY

A. GENERAL THEORY

Thin layer chromatography (TLC) and micro dry column chromatography (MDC) are techniques which form an extremely useful extension into the range of compounds where GC is no longer applicable because of low volatility, high polarity, or low thermal stability of the sample. TLC and MDC can be carried out at room temperature or below, and, since there is no transition to the vapor phase, volatility is not a factor which has to be considered.

B. CHARACTERISTICS

1. Sensitivity:

   The sensitivity is 10-20 μ of a compound.

2. Sample size:

   Sample size of 500 μ is typical.

3. Maintenance:

   Maintenance is negligible.

4. Cost:

   Instrumental cost is nil.

C. APPLICATIONS

TLC and MDC are usually employed where small samples of mixtures of sensitive or non-volatile compounds must be analyzed. It is, therefore, an extension of GC. These techniques are most widely used in the area of biochemical compounds.

VI. SUMMARY AND CONCLUSION

Instrumental capabilities of mass spectrometry, chromatography, the combined uses of both, thin layer, and micro dry column chromatography have been discussed in general terms. In conclusion, the author discusses how these techniques are used or can be used in the criminalistic laboratory, and how much of an investment would be required to equip such a laboratory with a GC/MS system.

PRINCIPLE OF A 180° DEFLECTION MASS SPECTROMETER

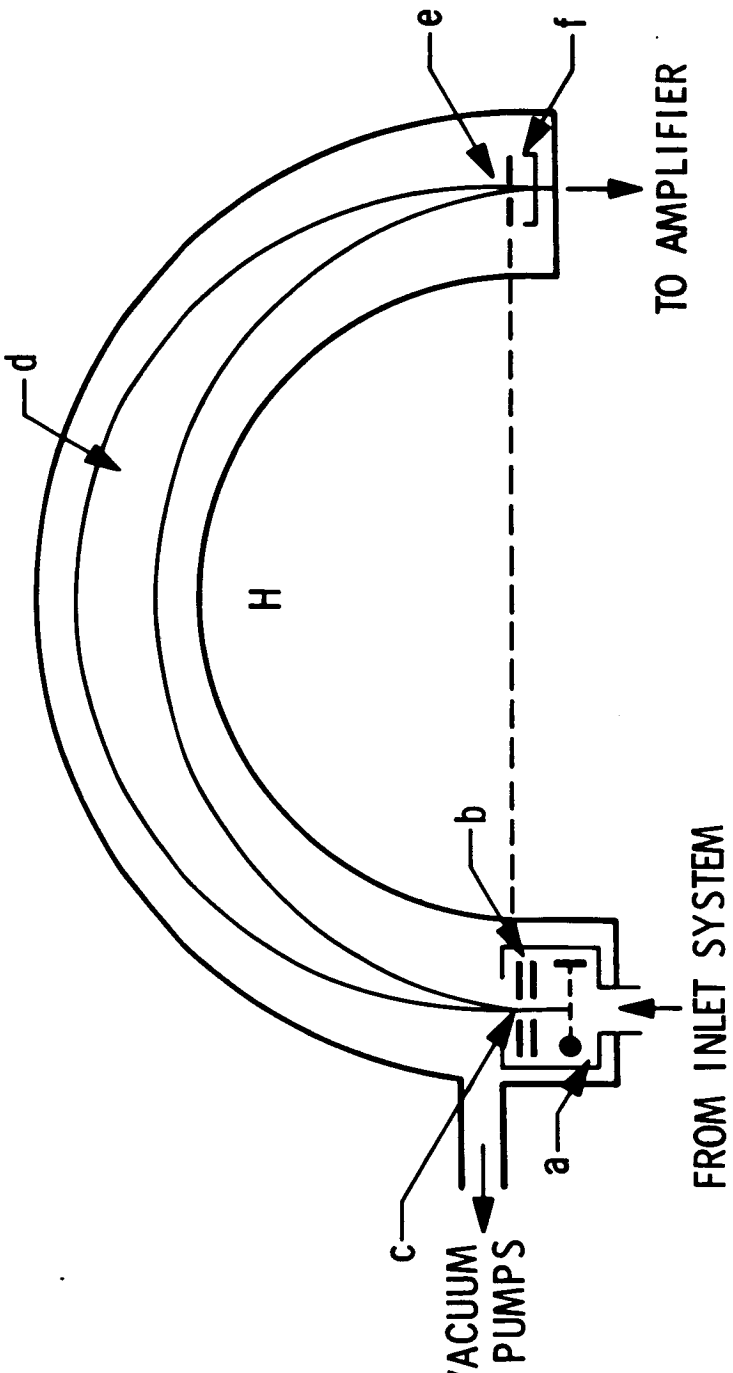


Fig. 4-1

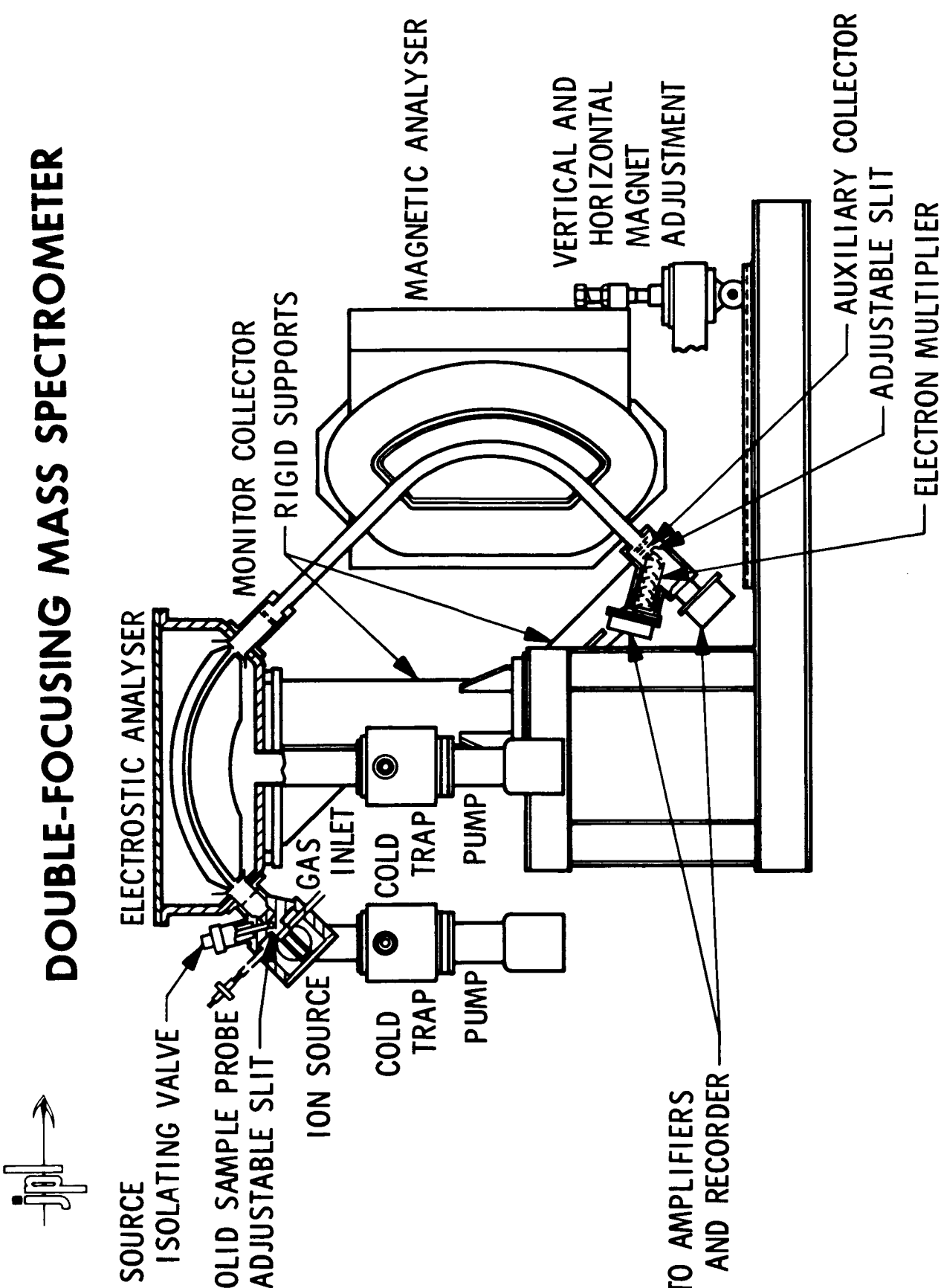

DOUBLE-FOCUSING MASS SPECTROMETER
SOURCE ISOLATING VALVE
SOLID SAMPLE PROBE ADJUSTABLE SLIT
ION SOURCE
GAS INLET
COLD TRAP
PUMP
COLD TRAP
PUMP
ELECTROSTIC ANALYSER
MONITOR COLLECTOR
RIGID SUPPORTS
MAGNETIC ANALYSER
VERTICAL AND HORIZONTAL MAGNET ADJUSTMENT
AUXILIARY COLLECTOR
ADJUSTABLE SLIT
ELECTRON MULTIPLIER
TO AMPLIFIERS AND RECORDER

Fig. 4-2

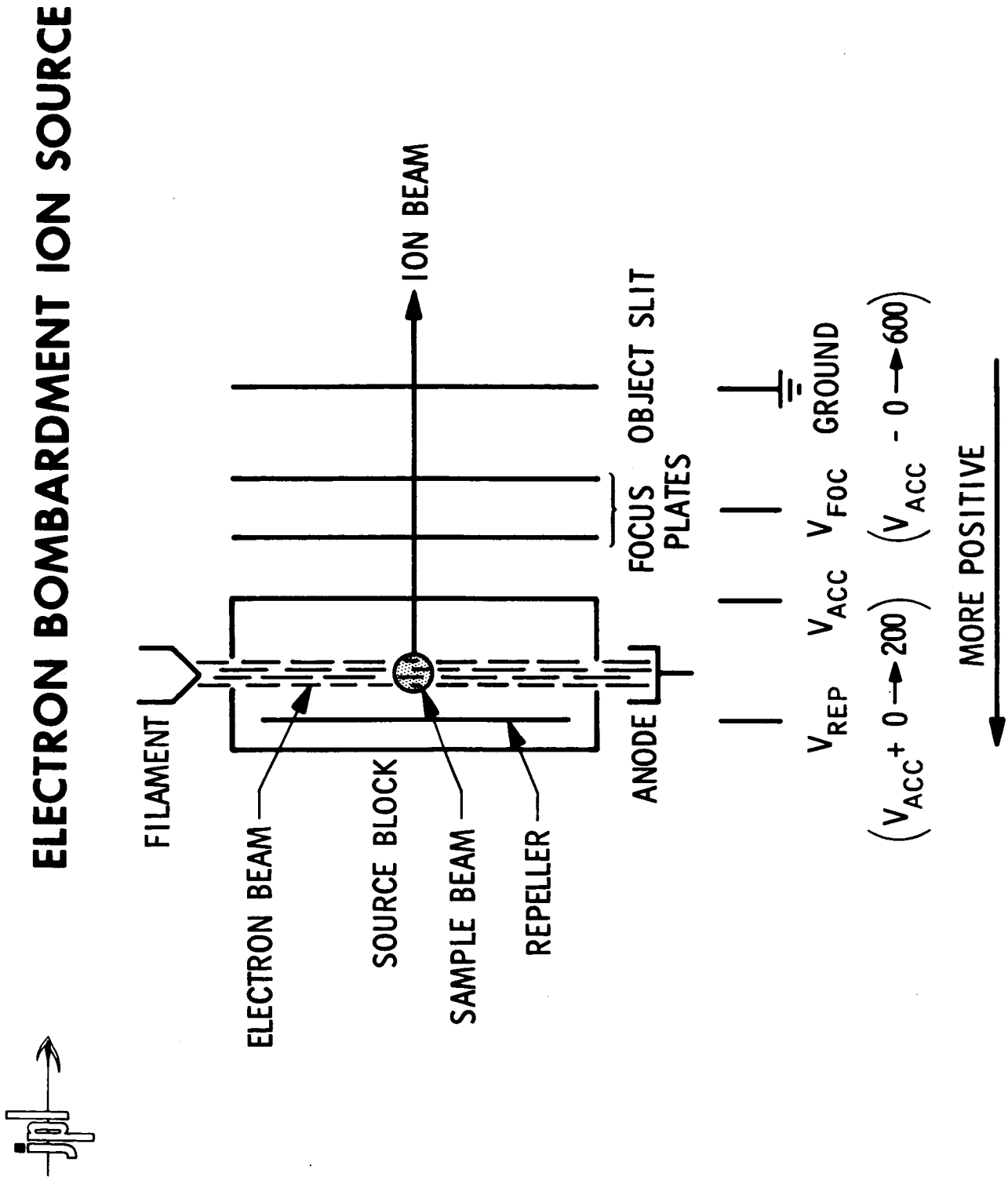

ELECTRON BOMBARDMENT ION SOURCE
FILAMENT
ELECTRON BEAM
SOURCE BLOCK
SAMPLE BEAM
REPELLER
ANODE
FOCUS PLATES
OBJECT SLIT
ION BEAM
V_{REP} V_{ACC} V_{FOC} GROUND
$(V_{ACC}+ 0 \rightarrow 200)$ $(V_{ACC} - 0 \rightarrow 600)$
MORE POSITIVE

Fig. 4-3

COMPOUND CLASSES ANALYZED BY MASS SPECTROMETRY

HYDROCARBONS
ALCOHOLS + DERIVATIVES
CARBONYL
ESTERS + LACTONES
ACIDS + ANHYDRIDES
ETHERS, ACETALS, KETALS, ORTHOESTERS
THIOLS, THIOETHERS, et al
AMINES, N. OXIDES, NITROSAMINES, AMMONIUM SALTS
AMIDES, LACTAMS
N - CARBONYL COMPOUNDS
CYANIDES
HALIDES
EPOXIDES
CARBONATES, CARBAMATES, UREAS, S-ANALOGS
NITRO COMPOUNDS et al
QUINONES
TROPONES, TROPOLONES
SULFOXIDES, SULFONES, et al
PYRIDINES, QUINOLINES
PYRAZINES, PYRIMIDINES
PYRROLES, ENDOLES
FURANES
THIOPHENES, BENZOTHIOPHENES
THIAZOLES, OXAZOLES, OXADIAZOLES, IMIDAZOLES, PYRAZOLES
ORG. PHOSPHOROUS COMP.
ORG. BORON COMP., BORANES, CARBORANES
ORG. SILICON COMP., SILANES, etc.
ORGANO METALLIC COMP. OF
- LITHIUM
- MECURY
- GERMANIUM
- LEAD
- TIN
- PLATINUM
- COPPER
- SILVER
- GOLD

Fig. 4-4

BIOCHEMICAL CLASSES ANALYZED BY MASS SPECTROMETRY

AMINO ACIDS + PEPTIDES

CARBOHYDRATES

ALKALOIDS

STEROIDS

LIPIDS (INCL. PHOSPHO LIPIDS)

NUCLEOTIDES, NUCLEOSIDES ETC.

TERPENES

ORGANIC PIGMENTS

- CHLOROPHYLS
- PORPHYRINS
- CAROTENOIDS

ANTIBIOTICS

INSECTICIDES, PESTICIDES, HERBICIDES

VITAMINS

Fig. 4-5

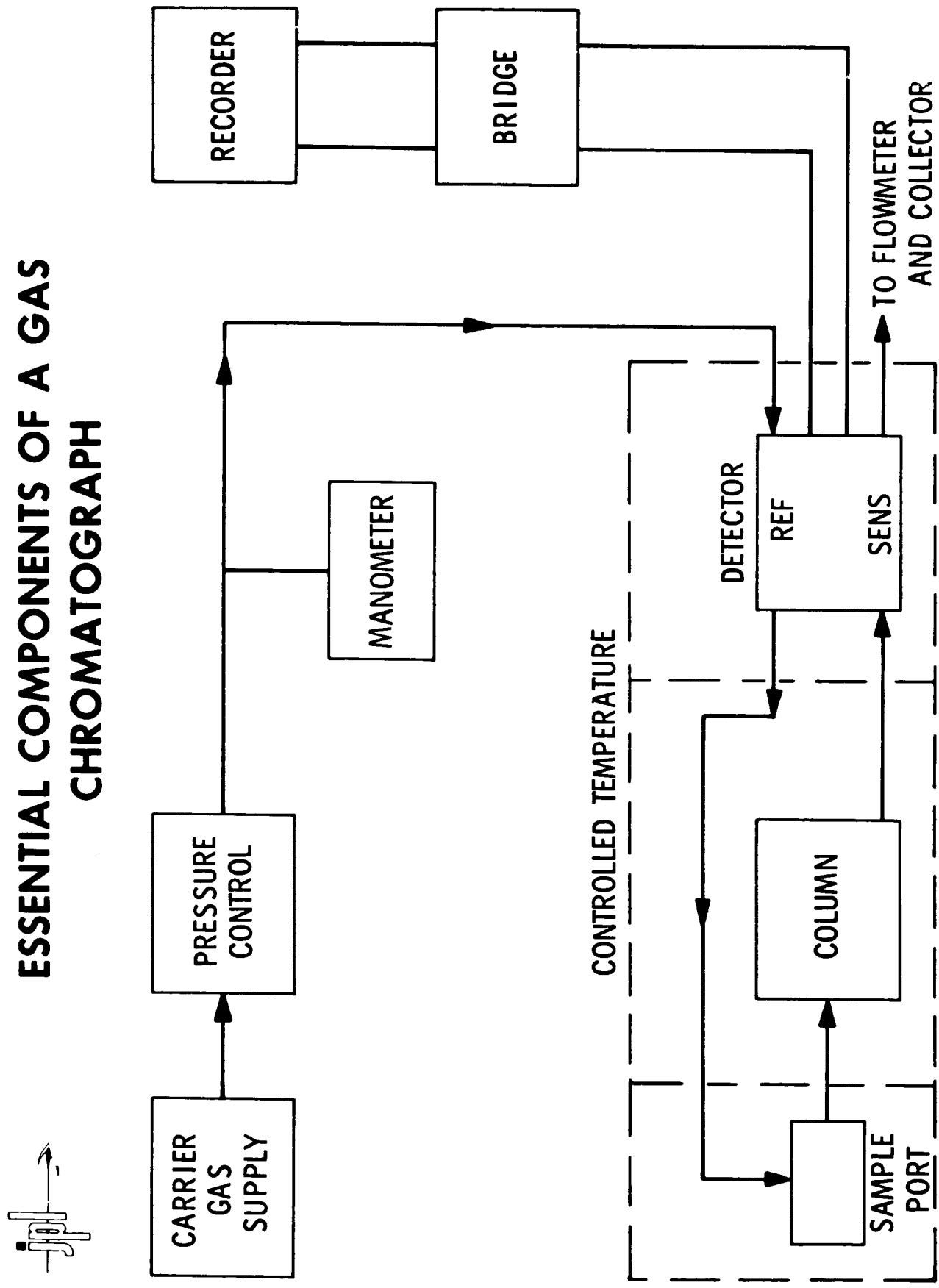

ESSENTIAL COMPONENTS OF A GAS CHROMATOGRAPH
RECORDER
BRIDGE
TO FLOWMETER AND COLLECTOR
MANOMETER
DETECTOR
REF
SENS
PRESSURE CONTROL
CONTROLLED TEMPERATURE
COLUMN
CARRIER GAS SUPPLY
SAMPLE PORT

Fig. 4-6

SIMPLIFIED SCHEMATIC OF A GAS CHROMATOGRAPH

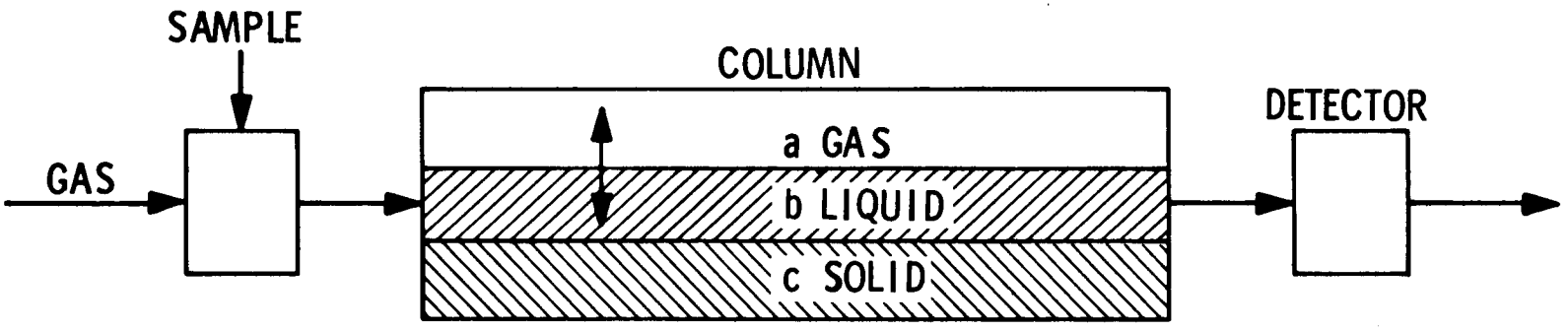


Fig. 4-7

SCHEMATIC DIAGRAM ILLUSTRATING ELUTION ANALYSIS

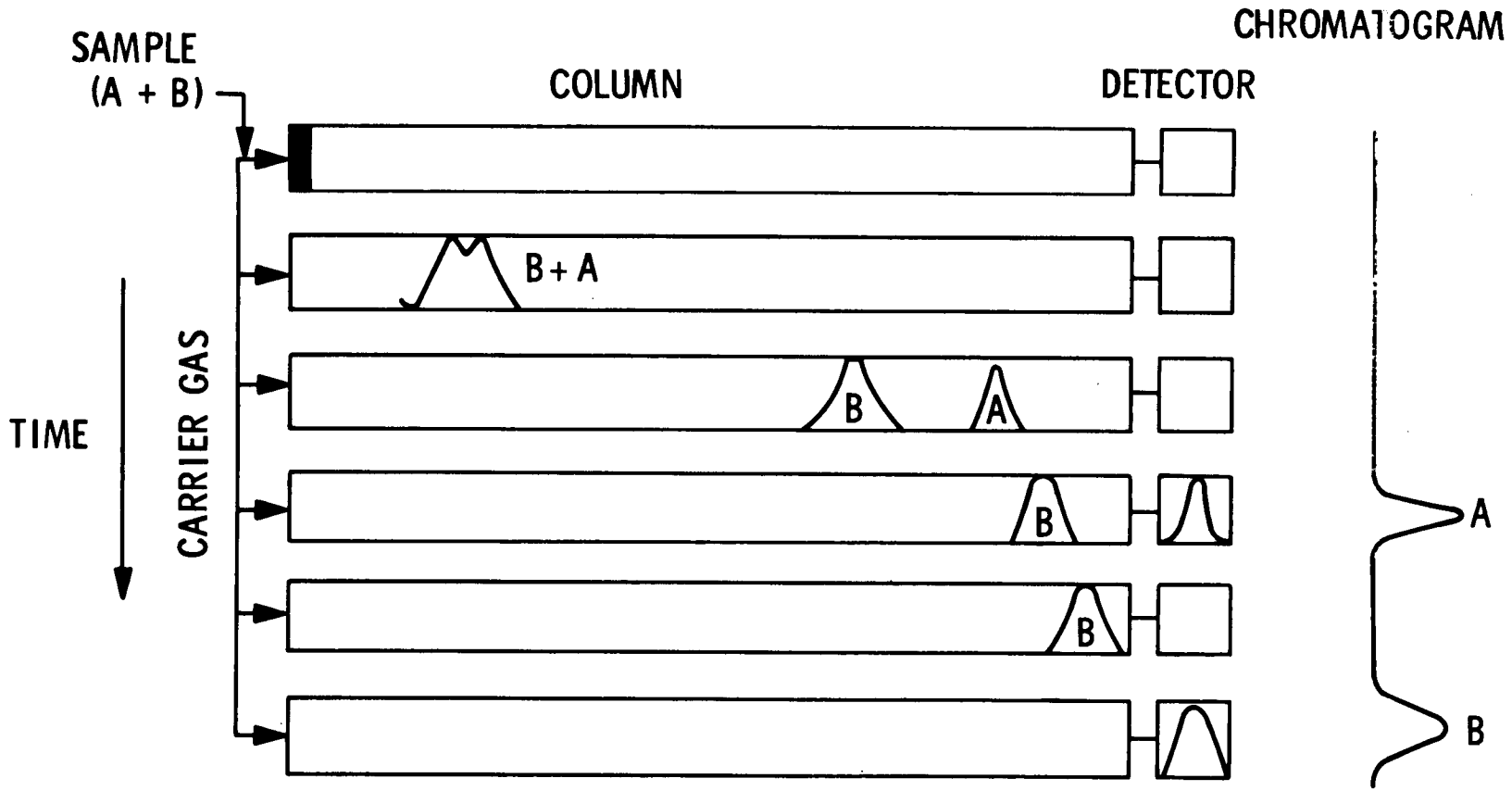


Fig. 4-8

GC/MS SCAN CONSIDERATIONS

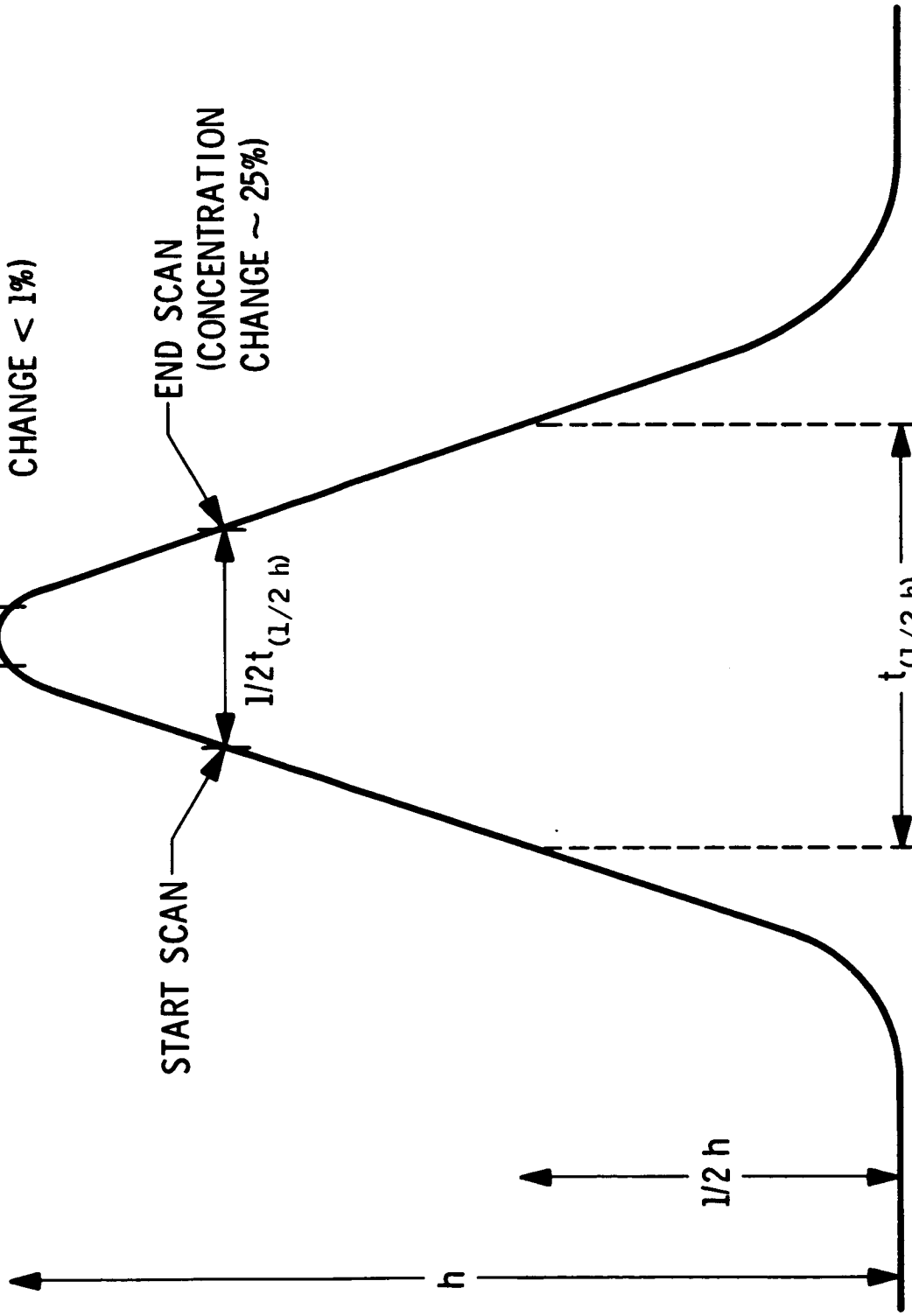


Fig. 4-9

THE ANALYSIS OF FOODS, FLAVORS, AND ODORS

COFFEE VOLATILES

COLLECTION OF FOOD VOLATILES

VOLATILES IN CHEESE

VOLATILE CONSTITUENTS OF BEER

FLAVOR CHANGES ON STERILIZATION BY IRRADIATION

FLAVOR OF PEARS

FLAVOR OF PEAS

FLAVOR OF COOKED BEEF

STRAWBERRY ESSENCE

ESSENTIAL OIL OF THE ORANGE

LEMON OIL COMPOSITION

DOUGH, OVEN GASES, AND BREAD

PESTICIDES ON VEGETABLES

HEAD SPACE GASES IN CANNED FOODS

Fig. 4-10

ANALYSIS OF FATTY ACIDS IN BIOLOGICAL MATERIALS AND FOOD STUFFS

HUMAN SERUM

HUMAN SEBUM

ADIPOSE TISSUE

SKIN SURFACE FAT

GAUCHER'S DISEASE CEREBROSIDES

BILE

EARWAX

PHOSPHOLIPIDS

FOOD PRODUCTS

MUTTON FAT

HERRING FLESH

MILK

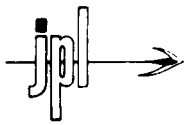
LIPIDS IN SPINACH

APPLE CUTICLE

PASTURE GRASS

NUTS AND OILS

Fig. 4-11



THE DETERMINATION OF PETROLEUM PRODUCTS

GEOCHEMICAL PROSPECTING

OIL EXPLORATION

FULL BOILING RANGE GASOLINES

C_1-C_7 HYDROCARBONS IN A SINGLE RUN

COAL TARS, PITCHES, AND NAPHTHALENES

EVALUATION OF CRUDE OILS

MERCAPTANS AND SULFIDES

RESOLUTION OF XYLENES

HIGH SPEED GC IN REFINERY OPERATIONS

MINIMIZING ANALYSIS TIME

JPL-STA 650-111

Fig. 4-12

APPLICATIONS IN BIOCHEMICAL, MEDICAL, HEALTH HAZARD AND LAW ENFORCEMENT PROBLEMS

SURVEY BIOCHEMICAL APPLICATIONS

AMINO ACIDS

BREATH ODOR

FACIAL ECZEMA FUNGUS

CHOLESTEROL LOWERING ACTIVITY

RELATION OF AGE AND RACE TO CHOLESTEROL ESTER PATTERN

ANAESTHETICS

CIGARETTE SMOKE

AIR POLLUTION

AUTOMOBILE EXHAUST

EYE IRRITANTS

WASTE TREATMENT CONTROL

BREATH ALCOHOL

BLOOD ALCOHOL

Fig. 4-13

ADVANCES IN ULTRAVIOLET AND INFRARED SPECTROSCOPY

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I. INTRODUCTION

A. HISTORICAL

A study of ultraviolet (UV) spectrographic methods was first published by R. W. Bunsen in 1861. In 1902, Coblentz recorded infrared (IR) spectra and recognized that organic materials have characteristic absorption bands. Good commercial IR and UV spectrometers became available about 1937.

B. GENERAL THEORY

Absorption spectroscopy involves the measurement of the interactions of electromagnetic radiation with matter whose wavelength lies between 0.2 μ and approximately 50 μ.

C. GENERAL APPLICATIONS

Absorption spectroscopy can be used to examine any non-metallic materials and, in some cases, even metallic substances.

II. CHARACTERISTICS OF ULTRAVIOLET, VISIBLE, AND INFRARED SPECTROSCOPY

A. PHYSICAL AND FUNCTIONAL PARAMETERS

1. Resolution involves two areas, wavelength and intensity. How well these can be measured is related to the quality and the type of instrument.

2. Repeatability:

   The repeatability is generally excellent.

3. Specificity:

   In the IR region, because of molecular motion, we have the effect that certain chemical groups give characteristic absorbancy bands or so-called group frequencies. In the UV, because it is electronic in nature and spectral bandwidth used is smaller, the amount of information is less in certain respects when compared to the IR region.

4. Quantitation:

   Quantitation depends on a large number of factors but, generally, 1 to 5% precision can be obtained.

5. Sensitivity:

   Three percent or less by weight of most materials can be seen. By absorbancy scale expansion and microtechniques, much lesser quantities can be detected.

6. Sample Preparation and Size:

   Sample preparation depends on whether the material is in a gaseous, liquid, or solid phase. In most cases, about 100 mg of sample is adequate. Some materials can be handled in lesser amounts.

B. OPERATIONAL

1. Time for Analyses:

   Most spectrophotometers can scan their full wavelength scale in 3 to 40 min. An average scan time is about 20 min.

2. Training:

   Junior College chemistry graduates can easily learn to operate most spectrophotometer systems in about one week.

3. Maintenance:

On well-designed systems, maintenance is minimal. Factory maintenance services are available and should be used except for very simple repairs. A spectrometer needs a clean, dry room and about 1 kw or less of 110V, 60 cycles of power. In some cases, cooling water and a flushing gas (nitrogen) are required.

C. COSTS

New instruments cost from $3,000 to $50,000, depending on the user's requirements. The availability of used instruments and some money-saving tips are discussed in a later section of the presentation.

III. APPLICATIONS

A. UV SPECTROSCOPY

Biochemists have long used UV spectroscopy in the study of nucleic acid derivatives. This method can easily be adapted to aid the criminalist in the quick identification of drug materials. Because of its electronic nature and narrow useful spectral range, the UV spectra region does not have the "fingerprint" capability that IR possesses ("fingerprint" in the sense that part of the spectra is typical of a given sample). A summary of the various parameters associated with spectroscopy is shown in Fig. 5-1.

B. RAMAN SPECTROSCOPY

Raman spectroscopy is a method which has been revived by neon helium laser technology. Raman spectroscopy has the potential capability of complementing present IR technology, but it has its own unique problems. Raman spectra can be obtained from aqueous samples. Solids or crystals can be used with special preparation. The present instrument costs about $22,000, a price which will probably drop as use of the instrument becomes more common in the near future. Raman spectroscopy can conceivably open an area of research of great value to the criminalist.

C. IR SPECTROSCOPY

Because of the broad applicability of IR spectroscopy, this technique is unique in its degree of versatility. The criminalist will find it far more useful than UV.

In the IR spectroscopy, aqueous samples can not be used because water has a very high absorptivity. Therefore, only neat or solids ground in potassium bromide or related salts give a spectrum without any interfering bands.

Spectra of gases in the IR region are very complex because of freedom-of-motion of the molecules. Solid and liquids have less degree of freedom-of-motion, so therefore the spectra have fewer absorption bands.

Group frequencies can be used for quantitative analysis of molecules or groups of molecules. At the present time, because of lack of experience, quantitative procedures are usually de-emphasized. Conceivably, they can be used in the criminalistic laboratory.

IV. CONCLUSIONS AND SUMMARY

Recent advances in UV and IR spectroscopy have many applications in the criminalistic laboratory. New methods in IR spectroscopy are extremely versatile. These methods can be applied by the criminalist to match an unknown sample with a known, to determine ratios of compounds, to measure an unknown concentration of a sample in a mixture, and to make quantitative analyses. A criminalist can use IR as a drug identification tool which allows him to identify almost every drug that can be presented.

The following articles are suggested for additional reading:

Potts, Jr., W. J. and A. Lee Smith. "Optimizing the Operating Parameters of Infrared Spectrometers", Applied Optics, Vol. 6, February 1967, pp. 257-265.

Whetsel, Dr. Kermit. "Infrared Spectroscopy", Chemical & Engineering News, Vol. 46, February 5, 1968, pp. 82-96.

Otvos, John W., Henry Stone, and W. R. Harp, Jr. "Theory of radiant-energy absorption by randomly discrete particles", Spectrochimica Acta., London: Pergamon Press, Ltd., 1957. Vol. 9, pp. 148-156.

Cunningham, K. G., William Dawson, and F. S. Spring. "Micro-determination of the Molecular Weights of Picrates, etc.", Analytical Chemistry, Easton, Pa.: American Chemical Society, Vol. 28, No. 10. October 1956. pp. 2305-2306.

Levi, Leo and Charles E. Hubley. "Detection and Identification of Clinically Important Barbiturates", Analytical Chemistry, Easton, Pa.: American Chemical Society, Vol. 28, No. 10. October 1956. pp. 1591-1605.

Wilks, Jr., Paul A. "Infrared Equipment for Teaching", Chemical Instrumentation, Vol. 46, No. 1, January 1969. pp. A-9 ff.

Lott, Peter F. "Recent Instrumentation for UV-Visible Spectrophotometry - Part 1: Dual-Beam Spectrometers, Part 2: Single-Beam Spectrophotometers", Chemical Instrumentation, Vol. 45, No. 2, pp. A-89 ff, February 1968.

SUMMARY OF SPECTROSCOPY

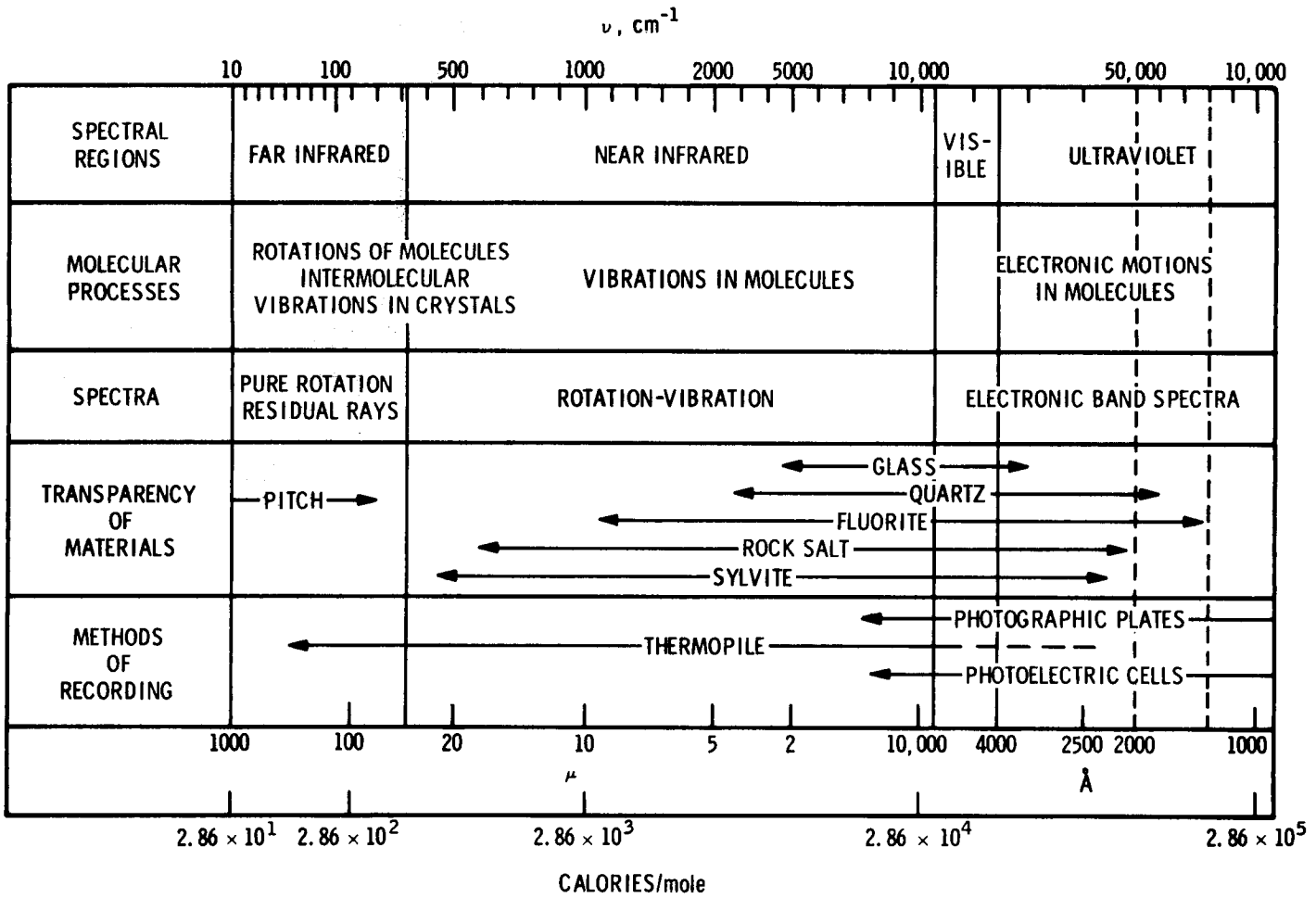

Fig. 5-1

SCANNING ELECTRON MICROSCOPY
APPLICATION POTENTIAL IN CRIMINALISTICS

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I. INTRODUCTION

A. HISTORY

Scanning electron microscopy is a method that, through the use of a Scanning Electron Microscope (S.E.M.), permits a better resolution and depth of field than optical microscopy.

The principles necessary for construction of an S.E.M. were proposed by M. Knoll in 1935. The first commercial instrument became available in 1965 from Cambridge Instruments, Ltd. of England as a result of research and development at Cambridge University under C. W. Oatley.

B. GENERAL THEORY

The S.E.M. detects and displays information derived from the action of an ultra-fine electron probe scanning a specimen surface in a square raster (see Fig. 6-1). The processed information is imaged on a cathode-ray tube (CRT) scanned in synchronism with the electron probe in a manner analagous to television.

C. BROAD APPLICATIONS

Among the varieties of information detectable are topographical details, surface potential distribution, subsurface conductivity, and luminescence.

The types of samples being studied include blood cells, algae, hair, fibers, insects, spores, botanical material, metal, paper, glass, paint, soil, organic polymers, and electronic components.

II. CHARACTERISTICS OF THE SCANNING ELECTRON MICROSCOPE

A. PHYSICAL AND FUNCTIONAL

1. Resolution:

   Resolution depends on the specimens and operating characteristics of each microscope, but it can be as good as a minimum of 100 Å. Depth of focus of the S.E.M. is always better than a light microscope by a factor of at least 300 (see Fig. 6-2). The magnification range is variable from X20 to a high of X100,000. Values up to X50,000 are generally useful; the higher values are used for focusing.

2. Repeatability:

   On the same or similar examples under similar operating parameters, the visual and photographic results should be similar.

3. Sensitivity:

   The sensitivity depends on the cleanliness of the sample surface.

4. Sample Size and Constraints:

   Sample size depends on the S.E.M. model and modifications. The sample can be a 1" x 1" x 1" cube or, with minor modifications, can include samples several inches on a side.

   Most non-conducting specimens require a conductive layer such as gold. Sample materials are basically the same as in optical microscopy excluding samples which cannot withstand a vacuum and those that require transmitted light.

B. OPERATIONAL

1. Analysis Time:

   Photographic output requires less than 5 minutes in some cases.

2. Training:

   No special training is required. A background in photography and optical microscopy is helpful, and experience in electronics is even more advantageous. Several days, at most, is needed for basic training.

3. Maintenance:

   The S.E.M. is a complex piece of electronic machinery, and many problems may arise. However, most manufacturers and suppliers provide maintenance contracts at a reasonable cost. In addition, experience has shown that the equipment is basically reliable.

4. Cost:

   The basic instrument costs about $70,000, and as yet there is no second hand market. There are about 40 or 50 laboratories in the United States where the investigator can have his work done. Some of these will lease time on their equipment and allow the investigator to do his own work in their facilities. Costs run $250/half day.

III. OPERATIONAL MODES

A. EMISSIVE MODE

1. Topographical Contrast:

   Low energy secondary electrons emitted from the surface by primary electron-probe excitation are drawn in generally curved trajectories to a detector where, after amplification, this signal directly intensity-modulates the cathode-ray tube. Images are closely similar to those formed by reflected light optical microscopy but with much greater depth of focus and much greater resolution. Details in reentrant holes and behind protruding surface features out of the direct line of sight of the detector are often visible.

2. Surface Voltage Contrast:

   Surface potential differences alter the trajectories of secondary emitted electrons, superimposing voltage contrast onto topographical contrast.

B. REFLECTIVE MODE: TOPOGRAPHICAL CONTRAST

By changing the detecting system bias or using another detector, high energy reflected primary electrons traveling in straight-line trajectories can be used to form the image. Such images show extreme contrast compared to the emissive mode, and reveal no details in shadows. Since high atomic number elements reflect more electrons than the lighter elements, the degree of contrast produced on an image of a flat surface will be partially dependent on the atomic numbers of the elements present.

C. ABSORPTIVE MODE: MISCELLANEOUS CONTRASTS

Specimen current caused by the primary beam is used to directly modulate the cathode-ray tube beam. The form of image contrast depends upon the balance between such factors as accelerating voltage, secondary emission detector bias, nature of the specimen, atomic number distribution, topography, and even specimen potential.

D. CONDUCTIVE MODE: CURRENT CONTRAST

Within semiconductors, the primary beam generates conductive currents dependent upon hole-electron pairs within depletion regions formed; for example, at p-n junctions when reverse biases are applied to the p-terminal. This current, after amplification, directly modulates the cathode-ray tube. The specimen acts as its own detector to provide conductive maps of regions below the specimen surface.

E. LUMINESCENT MODE: LIGHT CONTRAST

By imaging directly on a photo-multiplier tube, light emitted by luminescing specimens due to action of the electron beam can be used to form an image on the CRT.

IV. APPLICATIONS

A. LIMITATIONS OF LIGHT MICROSCOPY

Observations of the surface morphology of opaque objects are severely limited in light microscopy because, as magnifications increase, working distances become shorter and lighting becomes more difficult. Only on highly polished metallographic specimens, using oil immersion lenses, is it possible to achieve magnifications of X2500. However, typical specimens in criminalistics are usually neither flat nor polished.

B. CAPABILITIES OF THE S.E.M.

A limited objective examination of a number of typical physical evidence materials has been made to obtain a preliminary idea of the application potential of the S.E.M. to criminalistics. The following equipment was used:

Cambridge Stereoscan Electron Microscope with goniometer stage for rotation and tilt of the specimen and beam voltage varied from 5 kv to 20 kv.

Varian VE10 Vacuum Evaporator

AO Spencer Stereo Microscope

Leitz Metallurgical Microscope

Polaroid Type 55 Film

1. Samples:

The samples chosen for the feasibility study are objects in which surface morphology is of prime interest. These materials include:

a. Marihuana and other botanical leaves.

b. Paint flakes received in criminalistic cases.

c. Crossovers of ink lines and crossovers of ink and pencil lines.

2. Results:

a. <u>Marihuana:</u>

The marihuana examinations revealed surface details which have never been observed by light microscopy. Plate 1 (Fig. 6-3) illustrates the details seen on the cystolithic hairs

of the upper epidermis of a cannibis sativa leaf. Another unexpected feature was the fibrous-like surface detail shown in Plate 1c (500X). The electron micrographs shown on Plates 1a, b, c compared with the optical micrographs on Plates 1d, e, f demonstrate the superior effects obtainable with the high magnification, resolution, and depth of focus of the S.E.M.

b. Paint:

Paint flakes received in connection with police cases were examined at higher magnifications (9300X) than possible in light microscopy (see Fig. 6-4, Plates 2a, b). Surface structures revealed may serve as a new parameter for differentiation of this type of evidence.

c. Crossover Lines:

S.E.M. experiments have not yet been able to determine the order of writing of pencil on ink and ink crossover lines. However, the gold coating procedure makes easy the determination of the order of writing between ball pen and pencil crossovers (see Fig. 6-5, Plates a, b).

d. Other Specimens:

A few illustrations of other specimens are included to demonstrate the capabilities and potential applications of S.E.M.

(1) Shell 1, 22 cal pistol #1 (Fig. 6-6).

(2) Shell 2, 22 cal pistol #1 (Fig. 6-7).

(3) Shell 3, 22 cal pistol #1 (Fig. 6-8).

(4) Shown in Fig. 6-9:

(a) Eye of ant at 2100X (Plate 4a).

(b) Red blood cell at 17000X (Plate 4b).

(c) Microwire weld bond at 500X (Plate 4c).

(d) Microwire weld bond at 500X in optical micrograph (Plate 4d).

(5) 6.35 Beretta cartridge case (Fig. 6-10).

(6) 6.35 Beretta bullets (Fig. 6-11).

V. CONCLUSIONS AND SUMMARY

First results indicate the feasibility of further study of various specimens in forensic science which are useful as evidence. The ability to make observations at high magnifications of surface phenomena with such startling acuity opens a new door for the exploration of evidence evaluation.

A preliminary study of the use of the scanning electron microscope in general criminalistics is presented with demonstrations of resolution, focus and depth of field at both low and high magnifications. Advantages and constraints of the method are discussed and suggestions for further development are made.

CAMBRIDGE STEREOSCAN * ELECTRON MICROSCOPE OPERATING PRINCIPLES

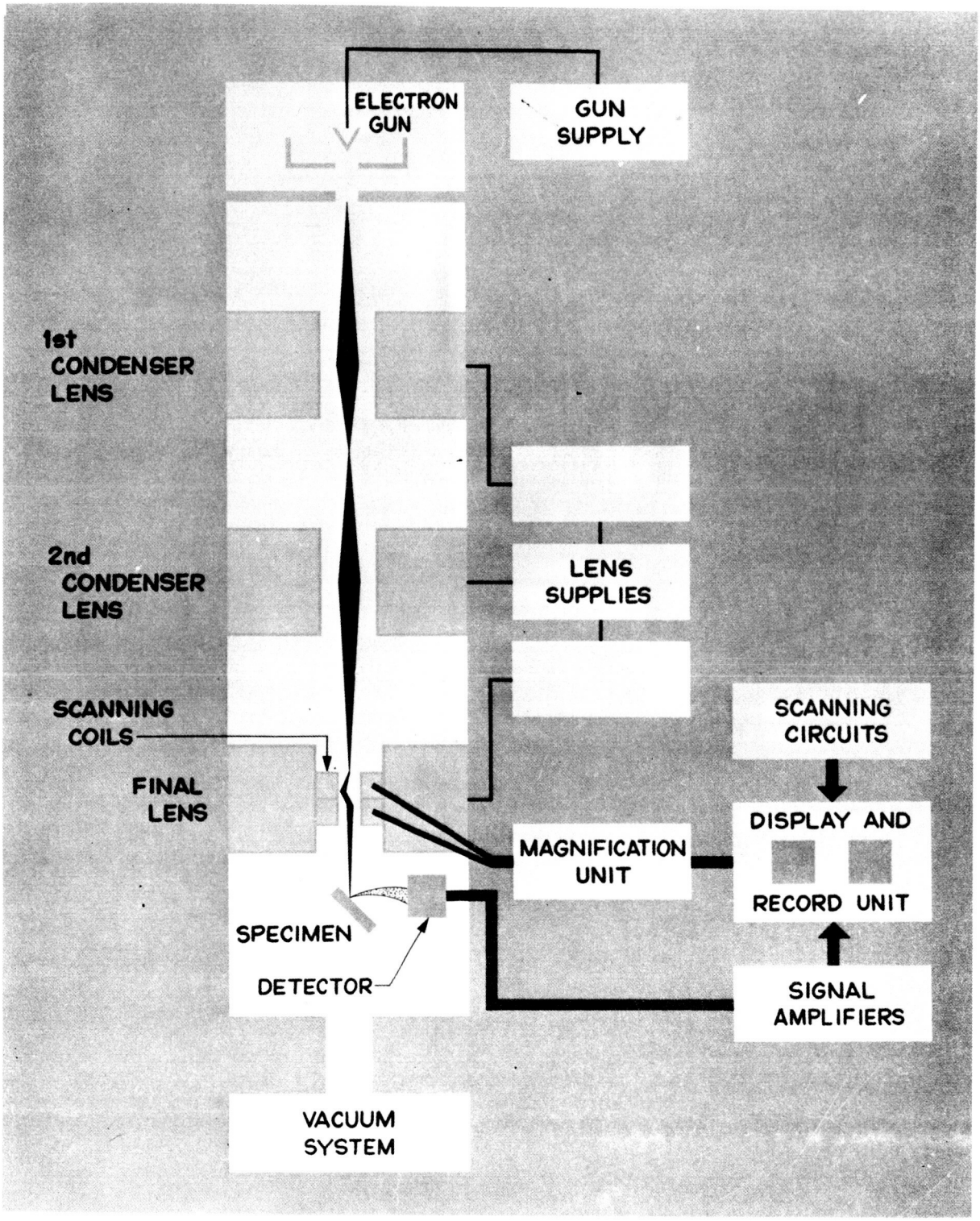
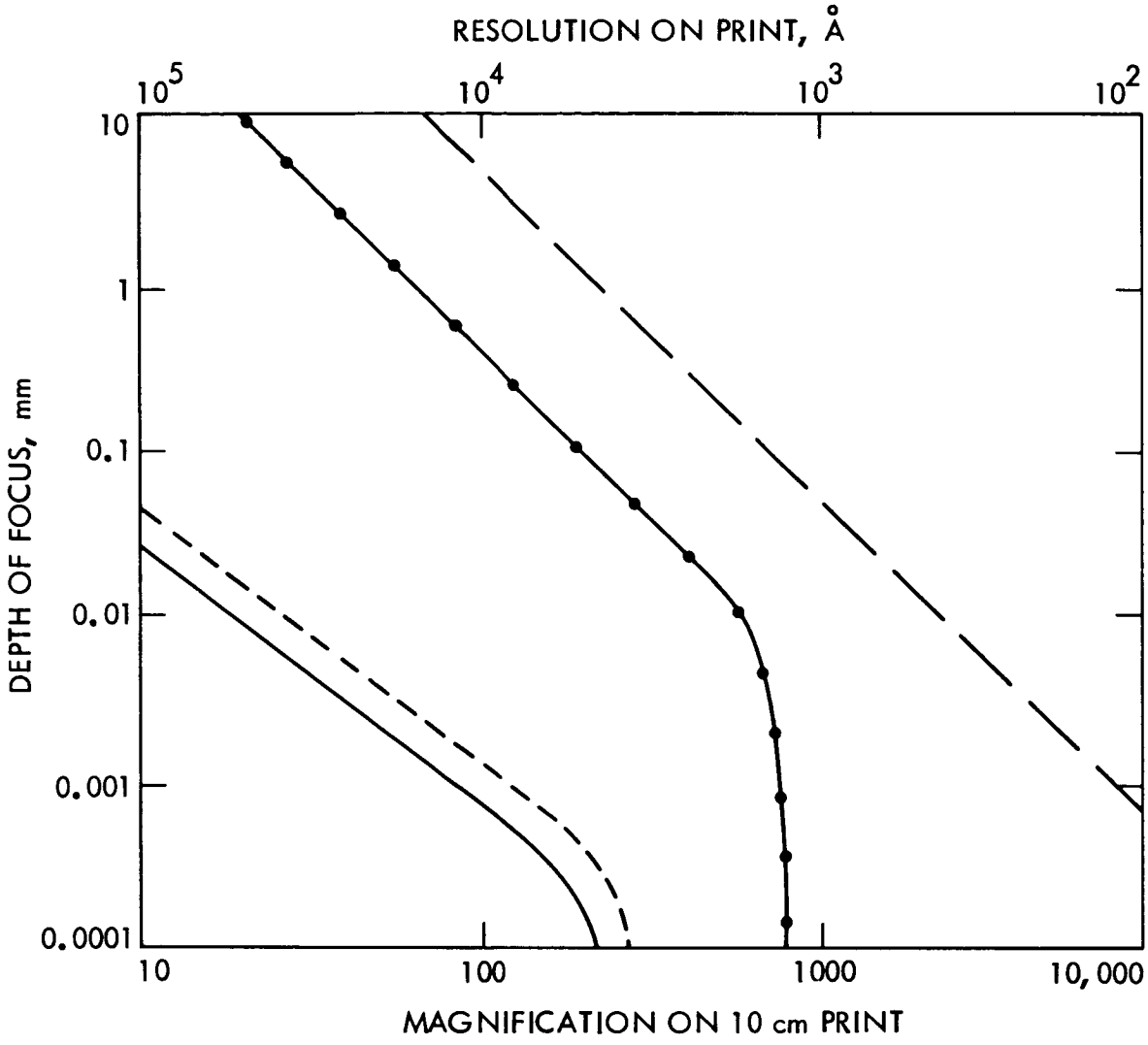
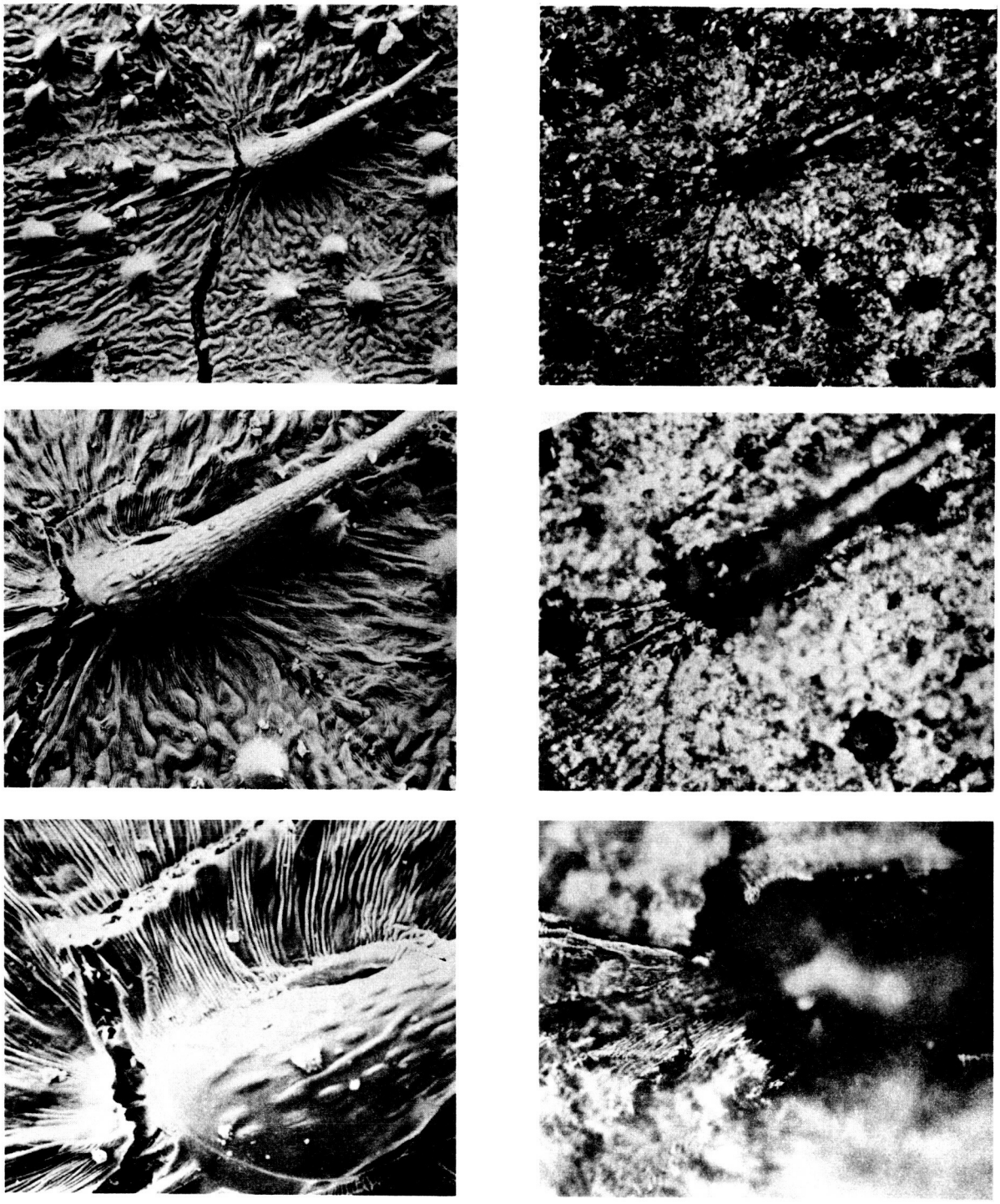


Fig. 6-1



RESOLUTION/DEPTH OF FOCUS GRAPHS FOR LIGHT MICROSCOPY AND S.E.M.

Fig. 6-2



Plates 1a, b, c, d, e, f. The plates in the left hand column (a, b, c) are of the upper leaf surface of a mature cannabis leaf viewed with an S. E. M. The magnifications in the original were 100X, 200X and 500X respectively. The plates in the right hand side (d, e, f) are at the same magnification and of the same region but they are optical micrographs. Both series are of a gold coated leaf surface.

Fig. 6-3

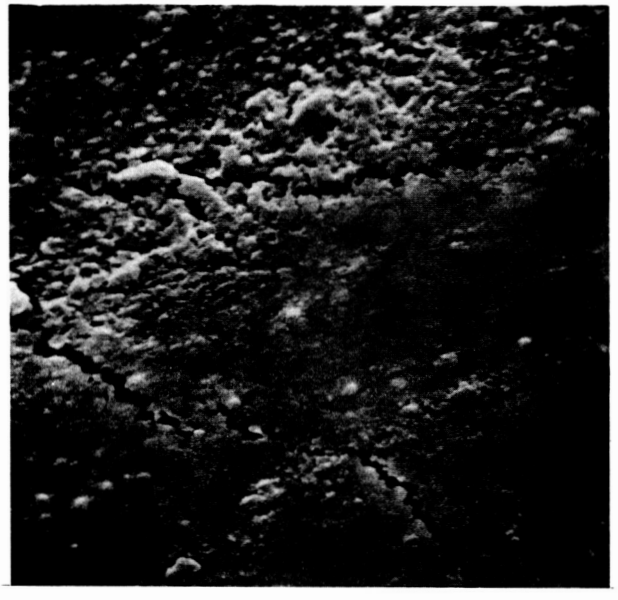


Plate 2A - 9300X
Sample A Paint Chip from source as Sample B

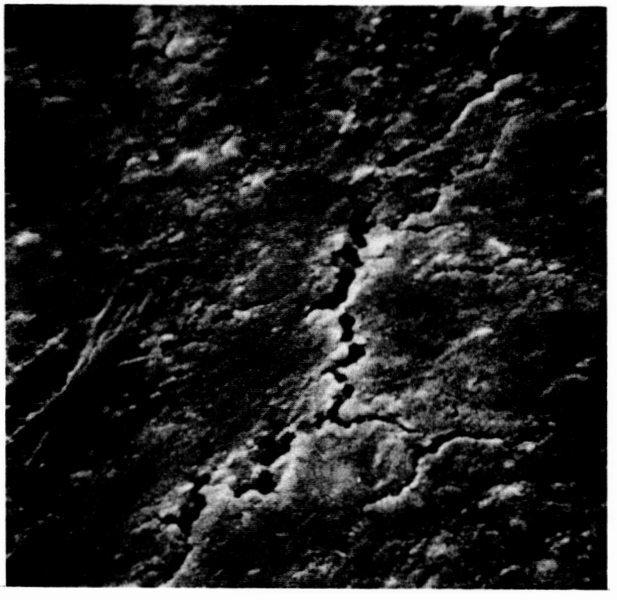


Plate 2b - 9300X
Sample B Paint Chip

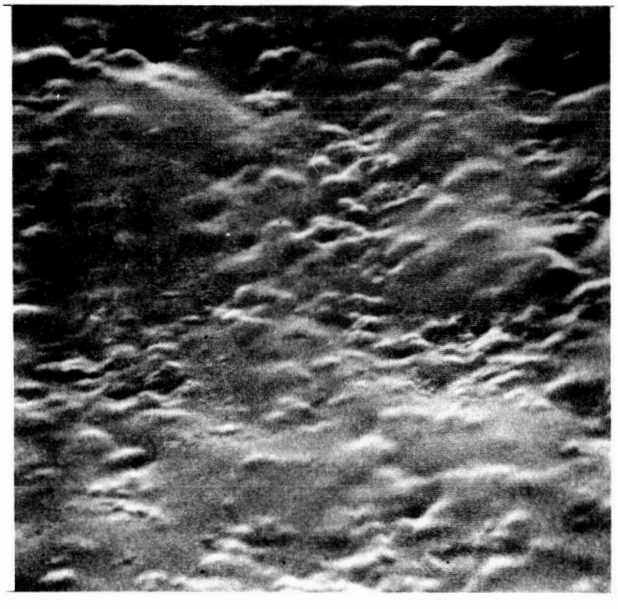


Plate 2c
Sample C Paint Chip from same source as Sample D

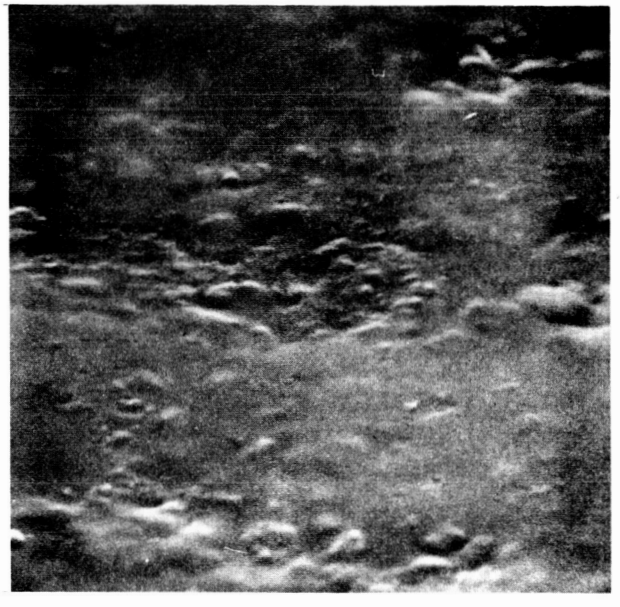


Plate 2d
Sample D Paint Chip

Fig. 6-4

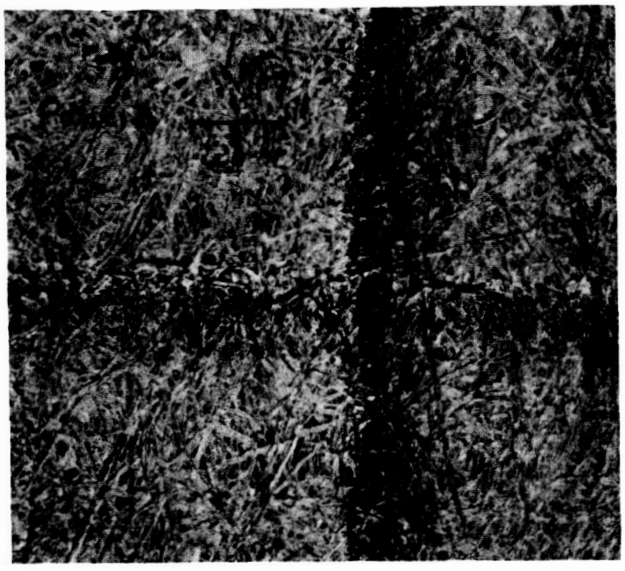


Plate 3a - 50X Optical micrograph of pencil over ball-pen ink after gold plating.

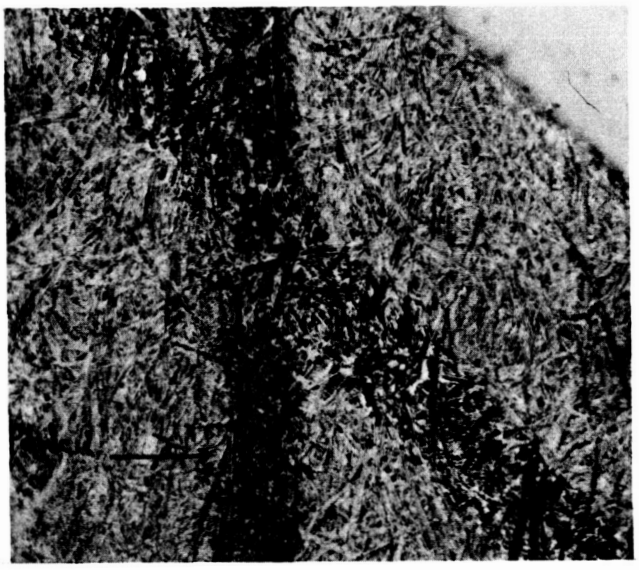
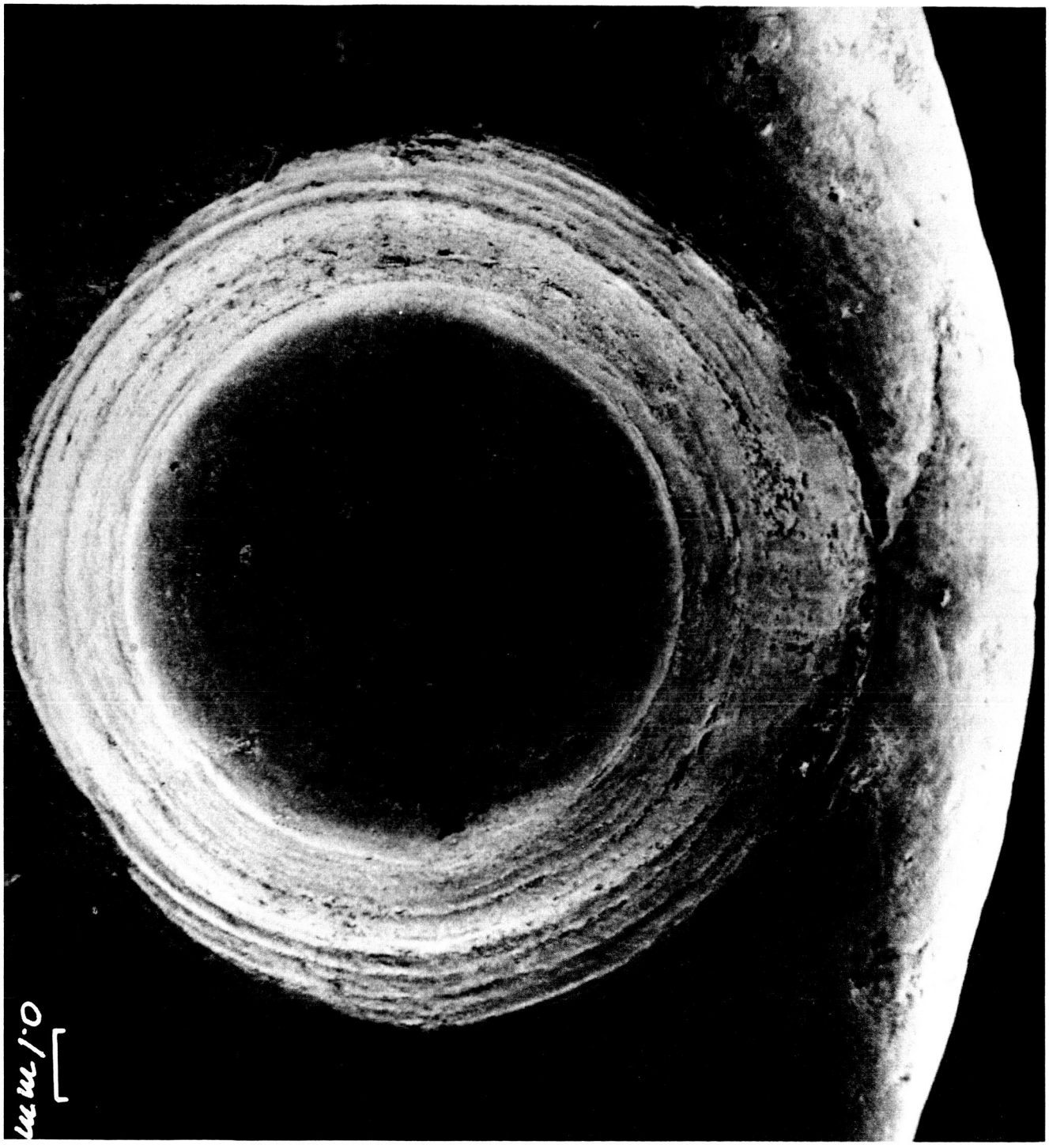


Plate 3b - 50X Optical micrograph of ball-pen ink over pencil after gold plating.

Fig. 6-5



60X | SHELL - 1 | 0°

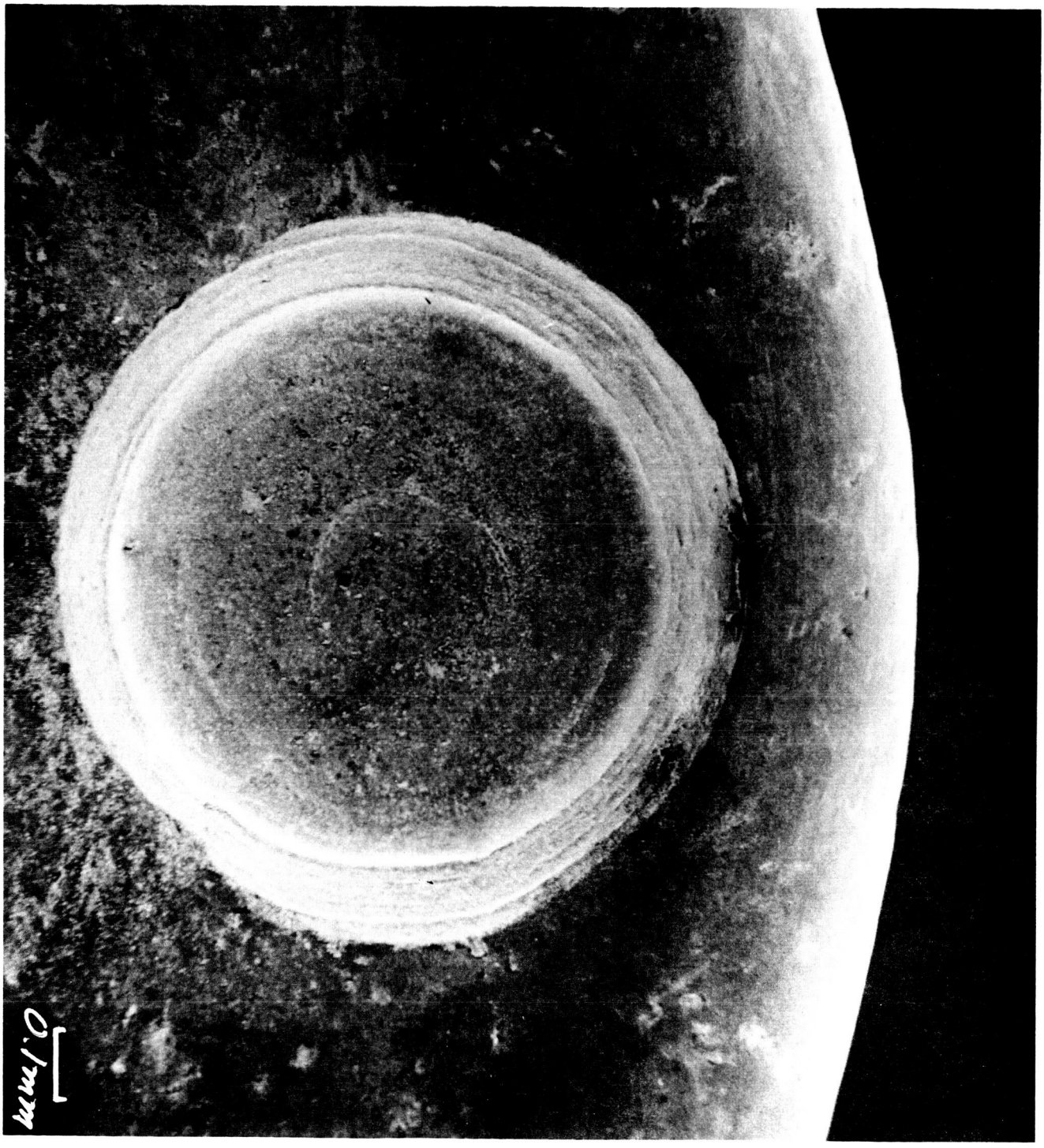
22 cal-pistol #1 | 10KV

Fig. 6-6

60X | SHELL-2 | 0°

22 cal-pistol #1 | 10KV

Fig. 6-7



60X SHELL-3 22 cal-pistol #1 0° 10KV

Fig. 6-8

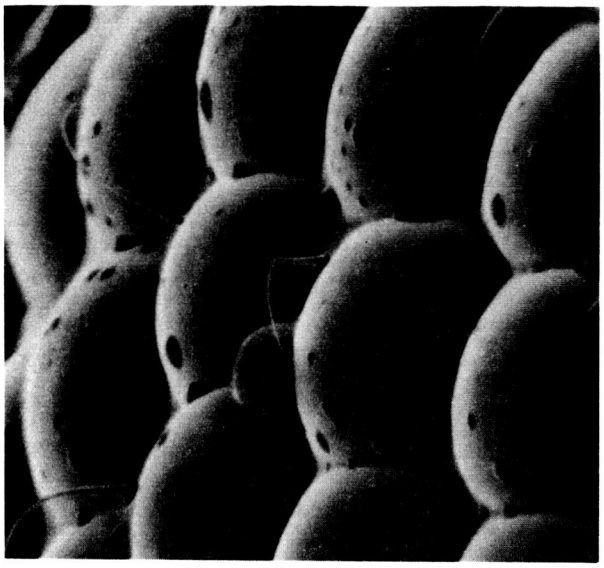


Plate 4a - Eye of ant at 2100X
Note, hairs between lenses.
Entomologists have never been
able to see this kind of detail
with light microscope system.

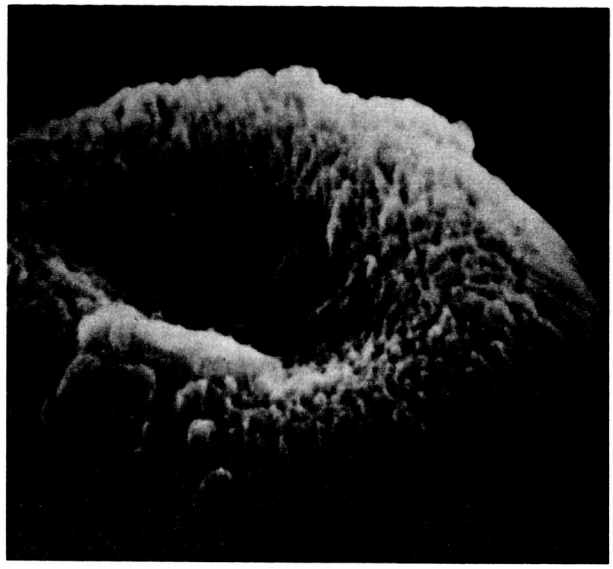


Plate 4b - Red blood cell at
17000X

Plate 4c - Microwire weld bond at
500X. Note cracks forming in ball.

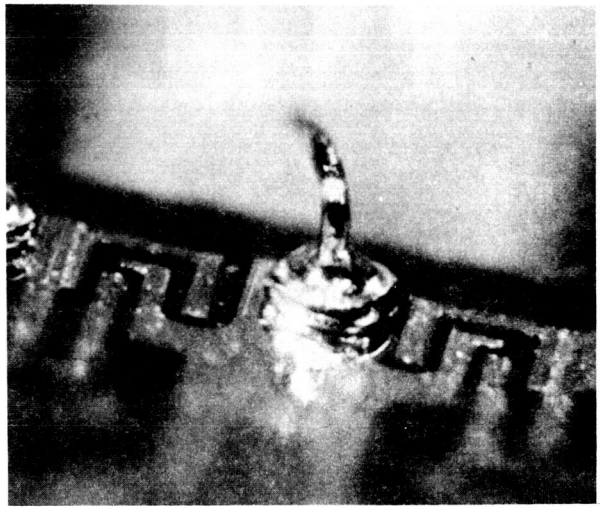
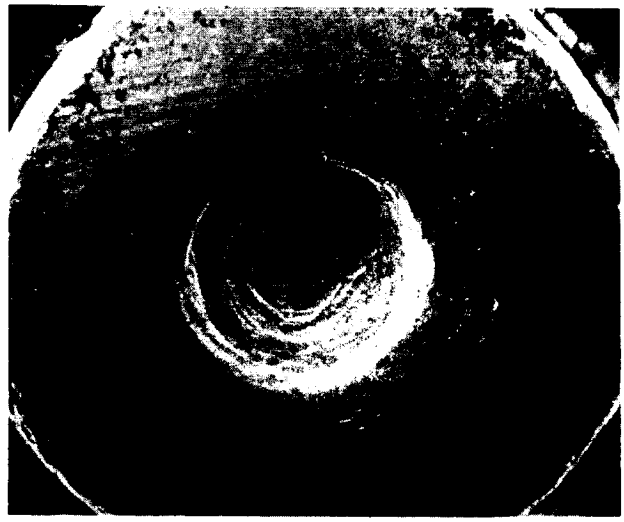


Plate 4d - Microwire weld bond
at 500X in optical micrograph.

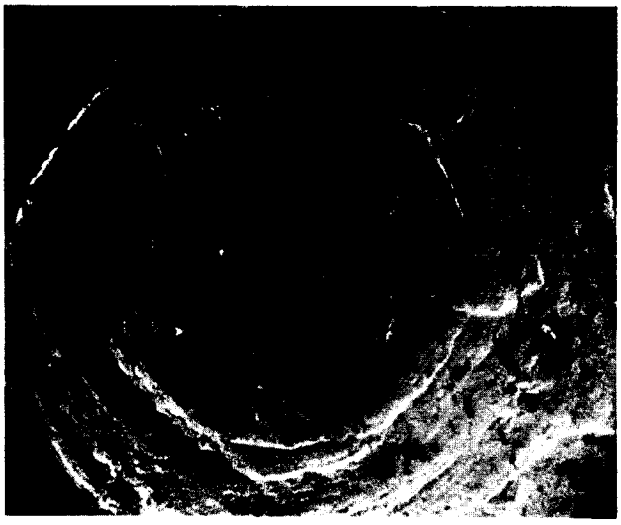
Fig. 6-9

6.35 BERETTA
CARTRIDGE CASE

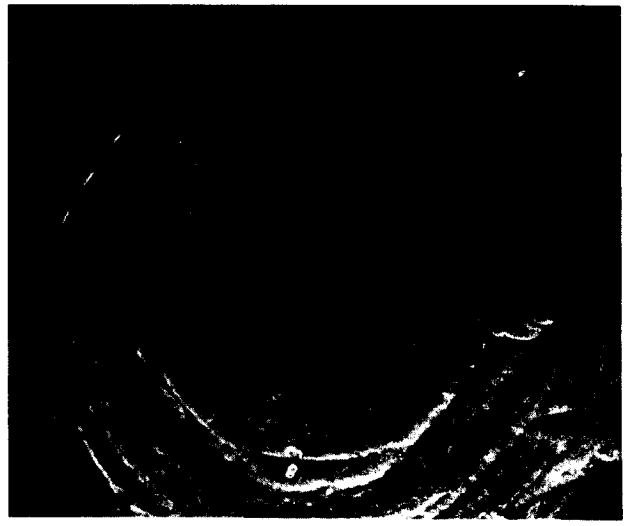
24X-0° SHELL A



24X-0° SHELL B



84X-0° SHELL A



84X-0° SHELL B

Fig. 6-10

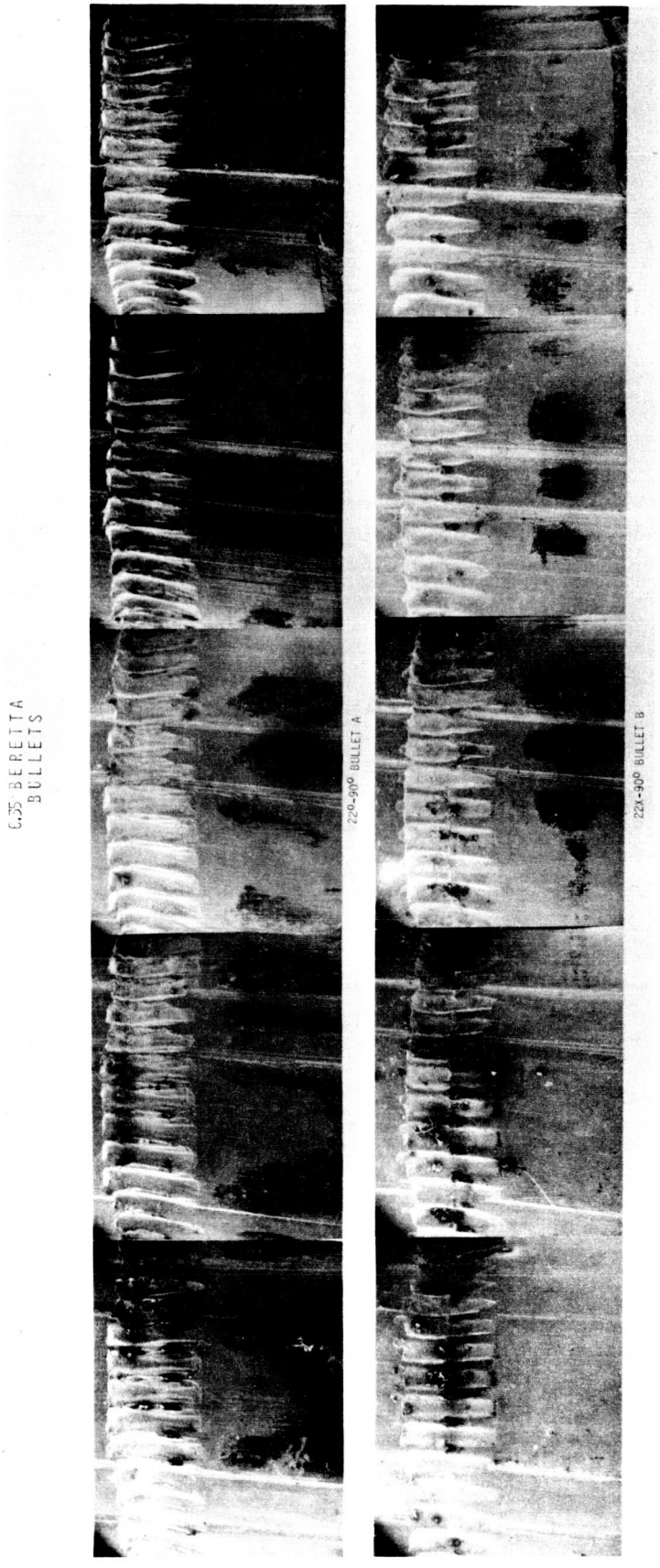


Fig. 6-11

COMPUTER APPLICATIONS

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I. INTRODUCTION

In this presentation, the author describes what a computer is, some of the things it can do, and some of the ways it can help the criminalist.

The term computer as used here refers specifically to a general purpose binary digital computer.

II. COMPUTER STRUCTURE, FUNCTIONAL

A. HARDWARE

A computer consists of input and output (I/O) devices, a control unit (also called a central processing unit or CPU), and a memory device (see Fig. 7-1). The CPU performs 4 functions: arithmetic, logic, movement of item, and transfer of control.

B. SOFTWARE

The program (software) is the list of instructions that tells the computer what to do. The program is stored in the memory and is executed by the control unit.

There are two types of programs, system programs and applications programs. System programs form an interface between a computer user and the computer hardware. Application programs are written by a user or programmer to do a specific task. The program is rarely written in machine language and requires a compiler to translate it into computer language. At least 3 steps are required in writing a computer program:

1. Analysis of the problem
2. Coding
3. Checkout

III. COMPUTER FROM A USER'S POINT

A. LARGE COMPUTER VS SMALL

While a small desk top computer sells from $2000 to $3000 (see Fig. 7-2), a large processing system costs several million dollars (see Fig. 7-3). The large computer, in addition to providing more I/O devices, more storage space, and more software than a small computer, has a larger memory, and its CPU can calculate faster. If the cost of computing is taken to be the number of calculations per second per dollar, a computer costing millions of dollars is cheaper than one costing a few thousand. To be economical, the large computer must be kept busy by many users, while the small desk computer may be used by one person.

B. TIMESHARING

Timesharing allows several users, each with his own I/O device (see Fig. 7-4), simultaneous access to a large computer.

The CPU cycles through all of the users' programs executing one at a time for a time slice of a few fractions of a second. Since the computer is incredibly fast, it appears to each user that it is operating entirely on his own program.

Charges for timesharing services are based on three things:

1. The time that a terminal is connected to the computer (connect time). This costs from $4.50 to $18 per hour.

2. The amount of CPU time used (a few cents per second).

3. Storage used for programs and data.

IV. SPECIFIC APPLICATIONS TO CRIME LAB

A. FILING AND REPORTING IN THE OFFICE

A minicomputer (see Fig. 7-5) or a terminal connected to a large computer can store case information, add new cases at any time, and automatically discard older cases or put them in an inactive file. The computer can answer queries about specific cases, tests, or analyses. The computer can also compile and print reports based on the data in the file.

B. SEARCHING AND RETRIEVAL IN THE LAB

In the case of an unknown (fingerprint, drug sample, bullet, etc.), the computer can be programmed to search the file to find a match or to present several "good" matches, leaving the final decision to the user.

C. DECISION MAKING

Research in progress today shows that the computer can make complex decisions. This is not done by exhaustive search through file data, but by modeling the decision processes of the user into the computer program.

D. CONCLUSIONS

While the basic concept and logic of the design of a computer is simple, it can complete very complex tasks. The quality of its output is totally dependent on the quality of the input. The computer can be used by the criminalist as a working tool in the office and in the laboratory.

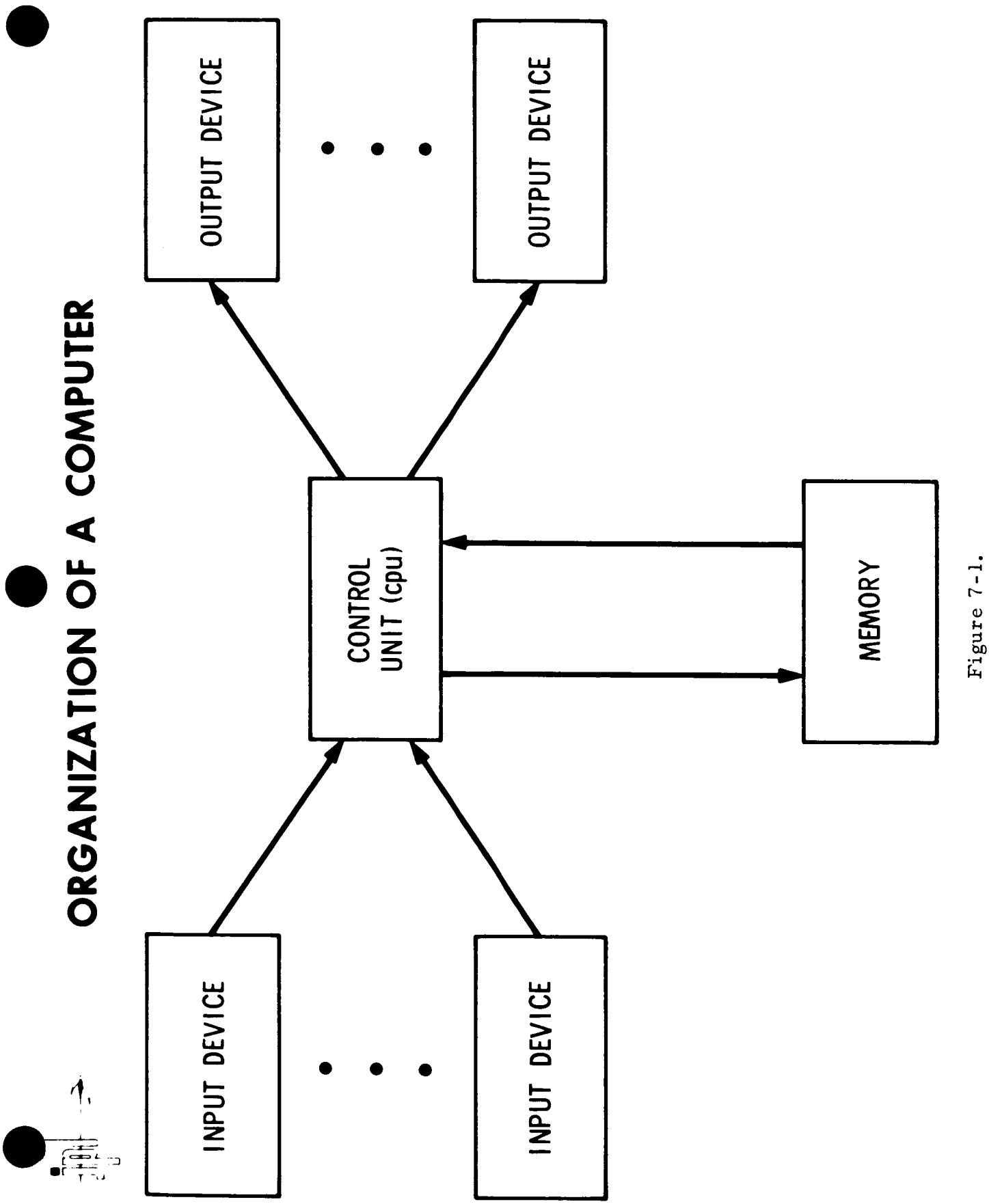

ORGANIZATION OF A COMPUTER
OUTPUT DEVICE
OUTPUT DEVICE
CONTROL UNIT (cpu)
MEMORY
INPUT DEVICE
INPUT DEVICE

Figure 7-1.

ELECTRONIC DESK CALCULATOR

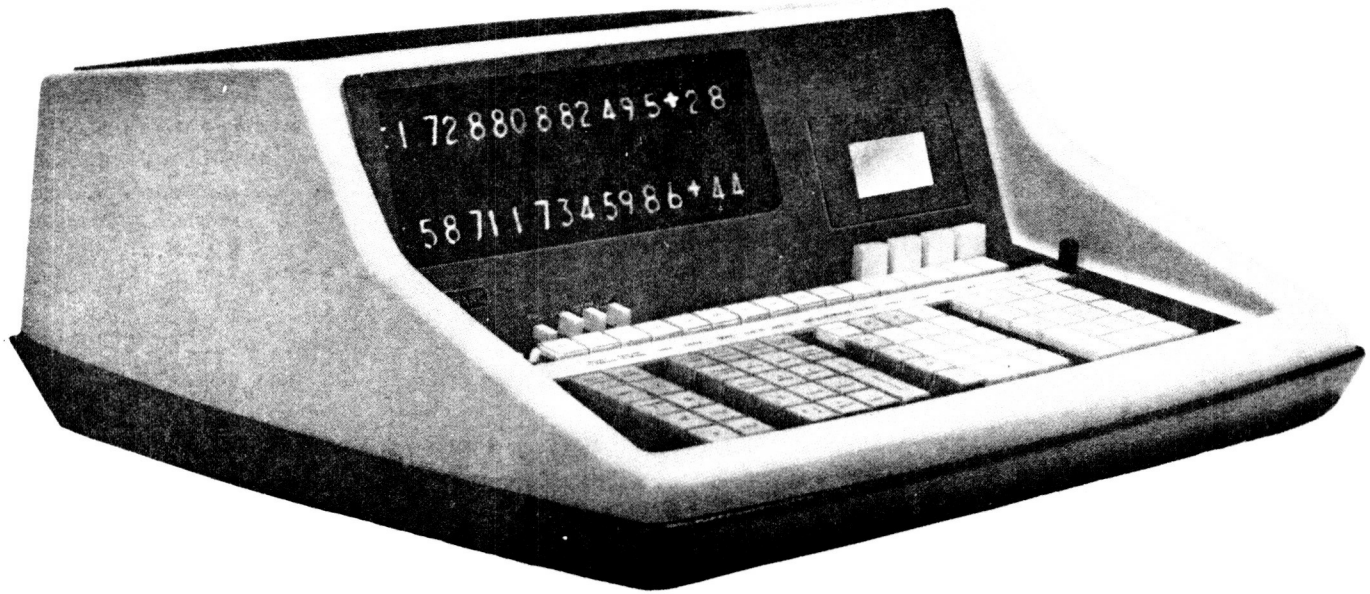


Figure 7-2.

LARGE COMPUTER INSTALLATION

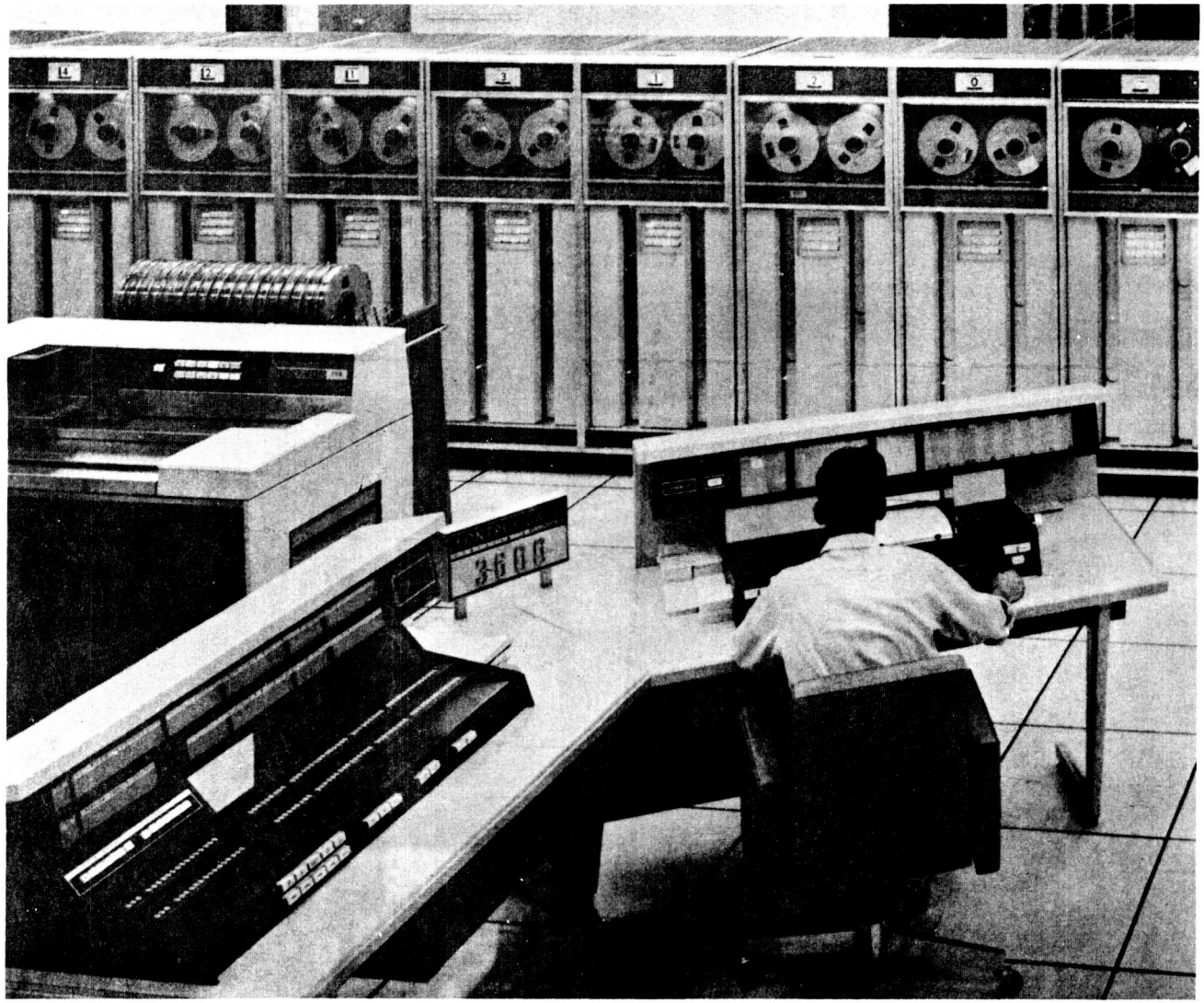


Figure 7-3.

TELETYPE TERMINAL

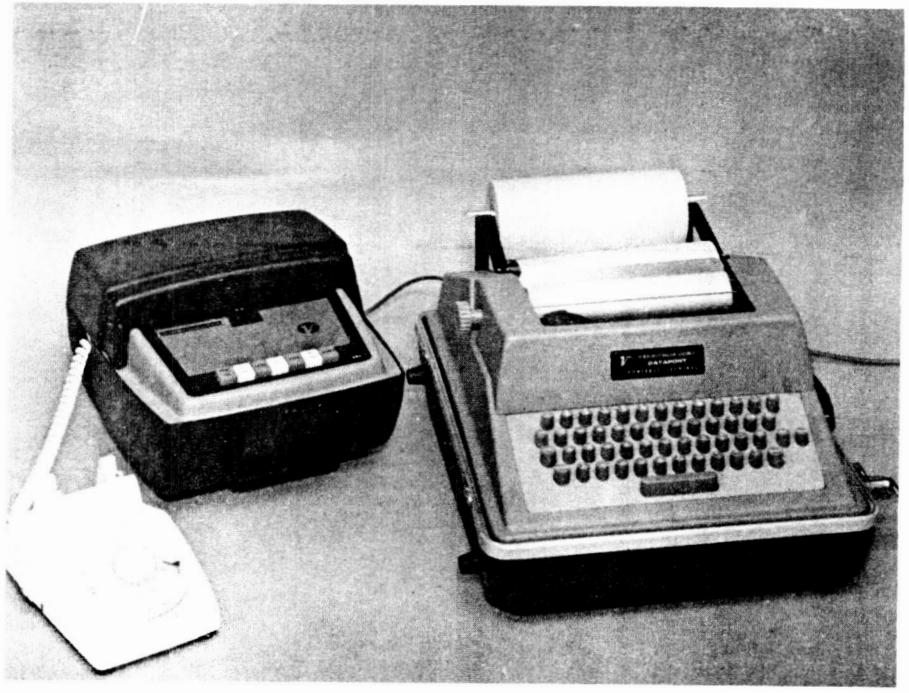


Figure 7-4.

MINI COMPUTER AND TERMINAL

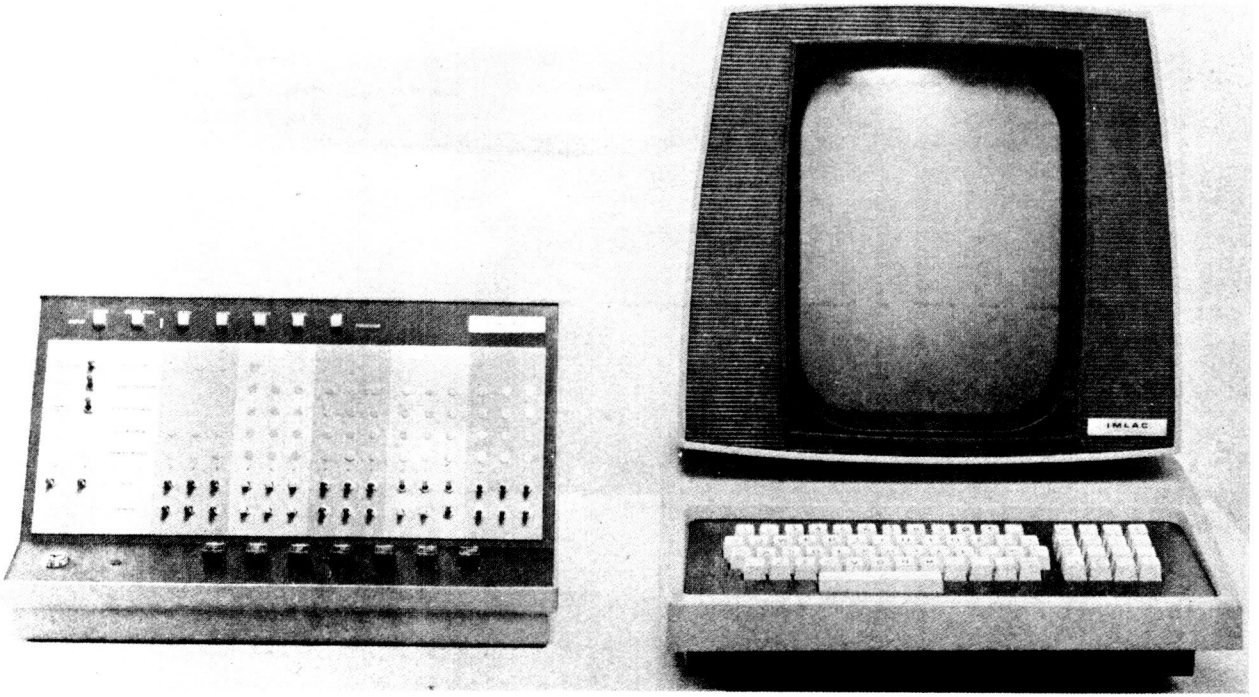


Figure 7-5.

FINGERPRINT IMAGE ENHANCEMENT BY COMPUTER METHODS

Richard J. Blackwell

Jet Propulsion Laboratory, California Institute of Technology
Pasadena, California

I. INTRODUCTION

A. GENERAL HISTORY

During the first half of 1969, investigations were initiated at the Jet Propulsion Laboratory to test the applicability of image processing techniques to some classes of criminalistic images. The preliminary results of one part of these investigations are presented in this paper.

B. GENERAL THEORY

The type of computer processing described here is termed image enhancement. The objective is to improve the image the viewer is seeing so that he may more easily and with greater reliability recognize a particular pattern or find the information he seeks.

C. BROAD APPLICATIONS

Digital computers have been used at JPL for several years to improve the geometry, photometry, contrast, and resolution of pictures received from

television cameras on board the Ranger, Surveyor, and Mariner unmanned spacecrafts. These computer methods developed in the space program have been successfully applied by JPL to image enhancement of medical X-ray films and biological microphotographs. A recent study demonstrates the feasibility of applying these same techniques to improving fingerprint images.

II. CHARACTERISTICS

A. PHYSICAL AND FUNCTIONAL

1. Resolution:

   The current resolution in terms of a spot of light ranges between 20 and 100μ.

2. Repeatability:

   Given the same image, the results will be identical.

3. Quantitation:

   A film negative can be digitized from 0 to 63. This is called a 6-bit digitization.

4. Sensitivity:

   Approximately a 1% change in film density can be detected. The film density optimum range is between 0 and 1.2.

5. Sample Preparation and Size:

   The current image size of a negative should be less than 50 mm in width and not greater than 80 mm in length.

B. OPERATIONAL

1. Time for Analyses:

   The time depends upon what kind of analysis is required, since computer time is directly proportional to the size of the picture.

2. Training:

   A basic knowledge of computers is required with a minimal amount of programming skills and some knowledge of photographic processes.

3. Maintenance:

Maintenance of computers is generally supplied by the manufacturer under a contract.

C. COSTS

Because of the high cost of computer equipment, it is advisable to rent time. Usually, the initial set-up for commercial scanning is $100 and $20 to $25 per million points. After this first charge, it costs $200/hr. for the use of the computer for the analysis itself. There is at least one commercial computer company in each large city. However, the degree of efficiency is not high as yet in commercially performed image enhancement.

III. SCANNING SYSTEM

The scanning system is the method for getting a picture into and out of a computer. The system used at JPL operates on the principle of measuring the amount of light which passes through a small area of the film at a given time. A film reader scans the film, a line at a time, much like a television camera does. Each point on the film is recorded on magnetic tape or sent to the computer as a series of numbers from 0 to 63 (white to black) which is proportional to film density at that point (see Fig. 8-1). After computer processing, the image is converted back into a picture by essentially the reverse of input scanning. The numbers representing the picture coming from the computer or from magnetic tape go to the scanner. Each sample produces a light beam whose intensity is proportional to the numbers. The light beam is then directed to unexposed film, and/or the picture data can go to a television monitor for direct display of the image.

IV. IMAGE PROCESSING GOALS

Four important techniques were developed during the growth of image processing technology for use in the space program:

1. Video Diagnostics:

Video Diagnostics is the analysis and display of signals coming from a camera or television system to ensure the best operation of the camera within the design limits.

2. Quantitative Restoration:

Quantitative Restoration or calibration is the technique of, first, recording the system noise and distortion which will change an input picture, and then, upon receipt of the real data, correcting it by the removal of all camera-introduced noise and distortion.

3. Subjective Enhancement:

   Subjective Enhancement is the technique of producing maximum discriminability for photo-interpretation by use of such processes as contrast heightening, edge sharpening, high and low frequency filters, etc.

4. Information Extraction:

   Information may be extracted at any time, depending upon what is sought. While the above steps were all employed in the space program, it is not necessary to proceed through all of them to compare two fingerprints.

V. FINGERPRINT IMAGE ENHANCEMENT

The technology developed for space photographs is directly applicable to fingerprint identification. Computer methods can be used to reduce the effects of under or over-inked fingerprints and poorly defined latents. In many cases, the information is there but cannot be seen by the unaided human eye nor detected by automatic classifiers. The procedure developed in this study was to produce a multi-directional derivative algorithm or slope detection routine which could readily recognize the successive ridge and valley structure and the minutia information inherent in all fingerprints, regardless of orientation. Upon recognition of such structure, the image is rescaled so that the contrast between the successive light and dark areas is evenly distributed. Under-inked areas are increased in contrast and over-inked areas are reduced.

Examples of latent and inked fingerprints are presented in which the original input image is shown and compared to its enhanced version. The procedure for film scanning and digital processing of images now in use at the Jet Propulsion Laboratory's Image Processing Laboratory is given. The following figs. illustrate the procedure:

Figure 8-2 shows the scan of an inked fingerprint recorded on clear acetate.

Figure 8-3, slope detection, shows how the method is used.

Figure 8-4 illustrates the method for scoring.

Figure 8-5 displays the scoring and intensity adjustments made.

Figure 8-6 illustrates the application of the program to the original fingerprint shown in Fig. 8-2 and a replot of the line after the program has increased the amplitudes.

Figure 8-7 shows the process again applied to a fingerprint on clear acetate.

Figure 8-8 illustrates the application of the process to a pair of fingerprints taken from a standard fingerprint card. The card was photographed, with no enlargement, and the film transparency scanned.

Figure 8-9 shows, on the left, an example set of latent fingerprints. The right hand side shows results of the enhancement process.

Figure 8-10 displays the original finger portion of a palm print taken from an arrest file fingerprint card. The lower half is the enhanced version.

VI. CONCLUSIONS

Imaging processing techniques developed for use in the space program have been successfully applied to medical X-ray films and biological micro-photographs. Recent studies indicate that fingerprints can be enhanced by utilizing the technique of maxima/minima detection. It may be desirable to use this technique as a preprocessing step prior to classification of fingerprints by automatic or semi-automatic equipment. Image enhancement is also valuable in special cases of individual inked or latent prints where insufficient minutia information can be obtained by normal photographic processes.

VIDEO FILM CONVERSION

PICTURE ELEMENTS (PIXELS)

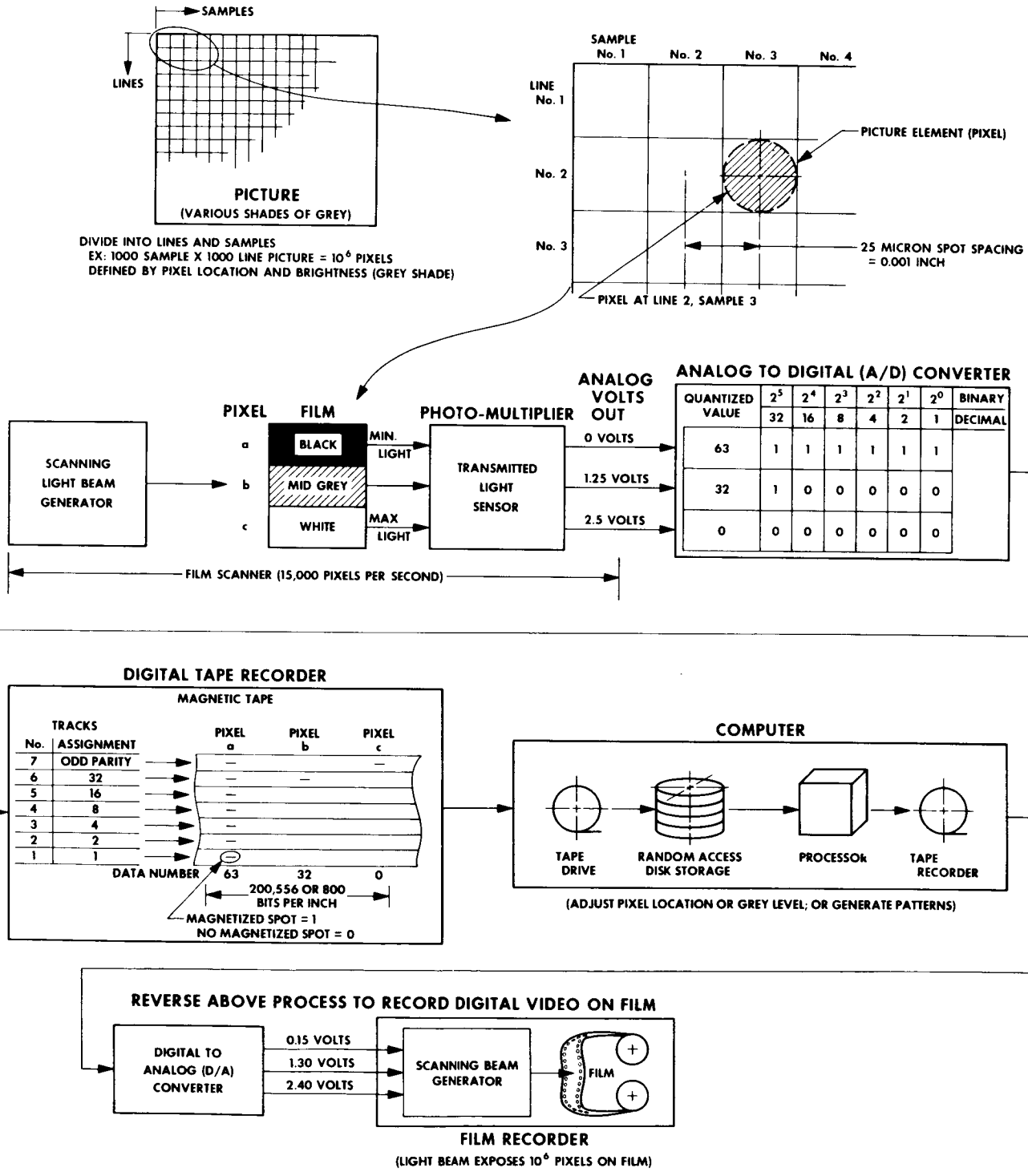


Figure 8-1.

SCAN OF INKED FINGERPRINT ON ACETATE

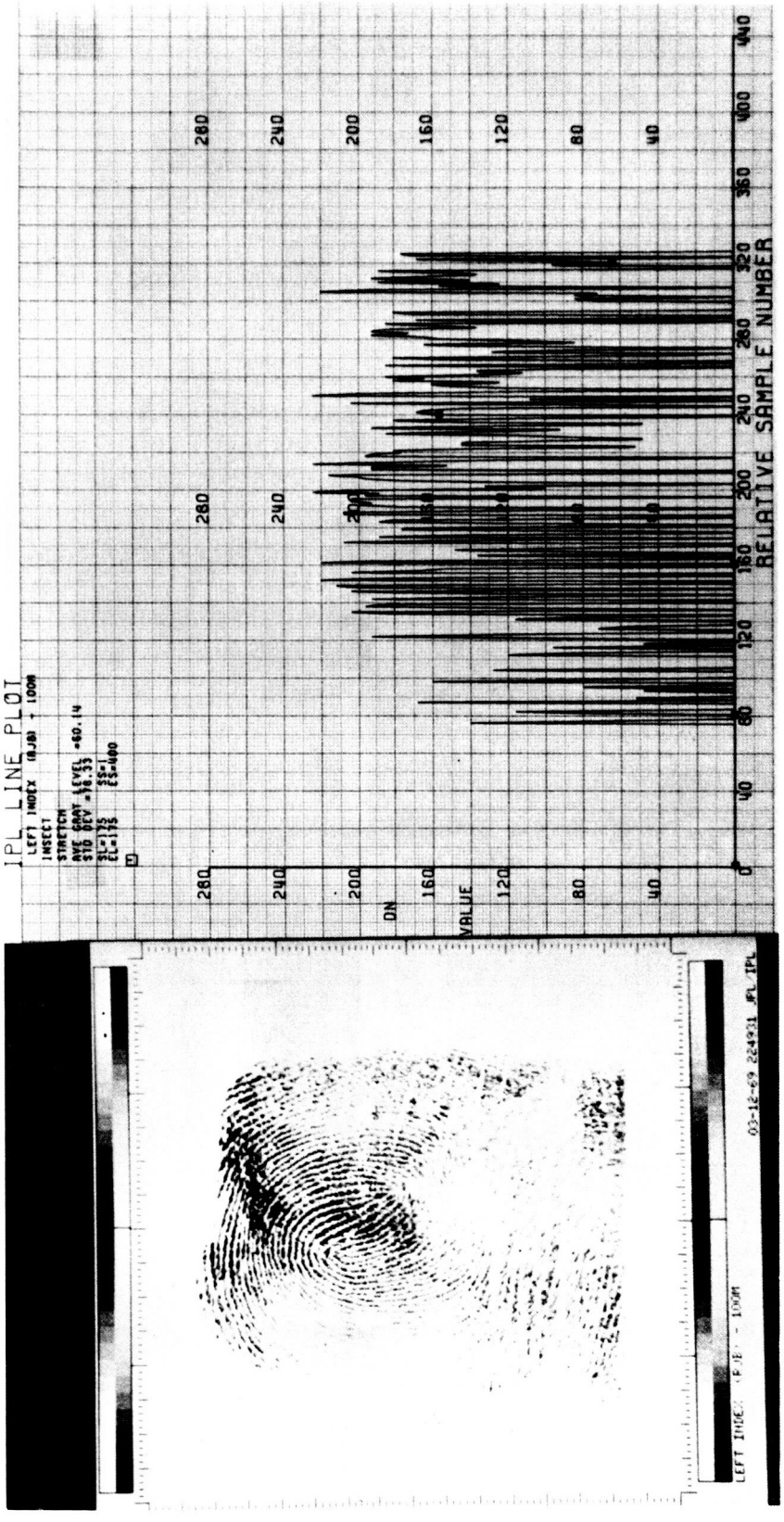
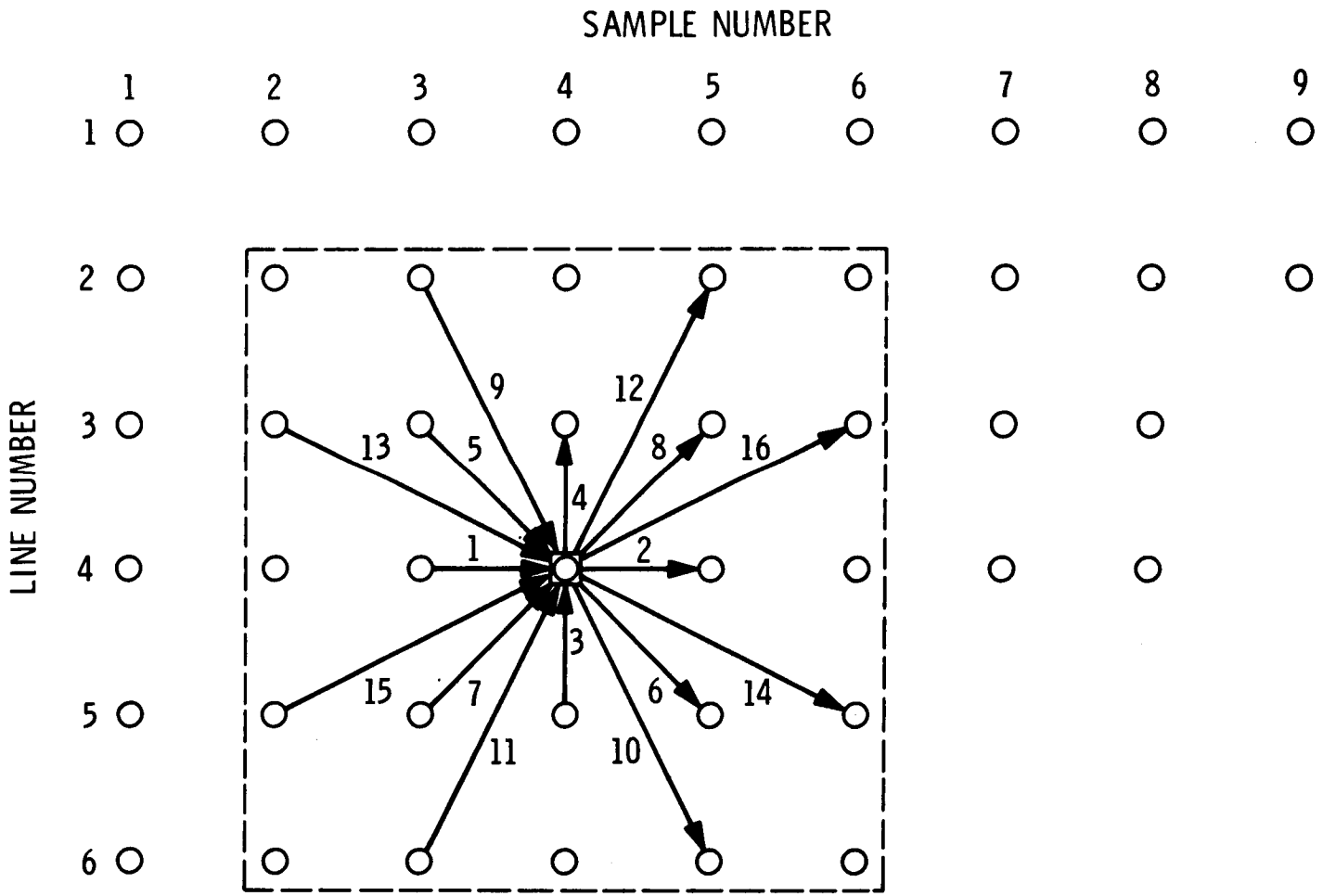


Figure 8-2.

SLOPE DETECTION



EXAMPLE

#15 (LINE 4, SAMPLE 4) - (LINE 5, SAMPLE 2) = - OR 0 OR +

#16 (LINE 3, SAMPLE 6) - (LINE 4, SAMPLE 4) = - OR 0 OR +

Figure 8-3.

METHOD FOR SCORING

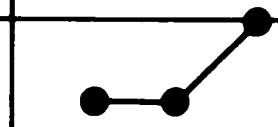
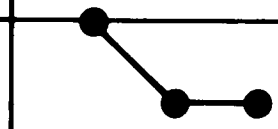
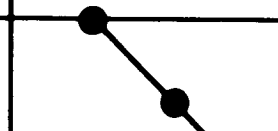
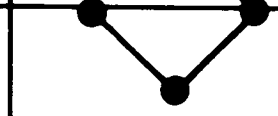
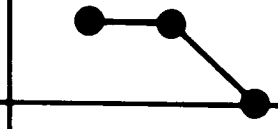
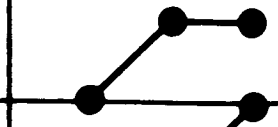
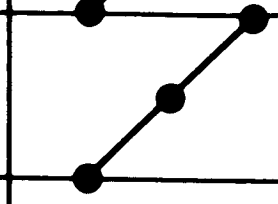
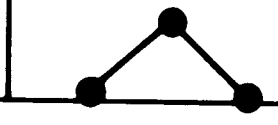
	1 2			MINIMUM	MAXIMUM
1		0, 0		0	0
2		0, +		2	
3		-, 0		2	
4		-, -		1	
5		-, +		3	
6		0, -			2
7		+, 0			2
8		+, +			1
9		+, -			3

Figure 8-4.

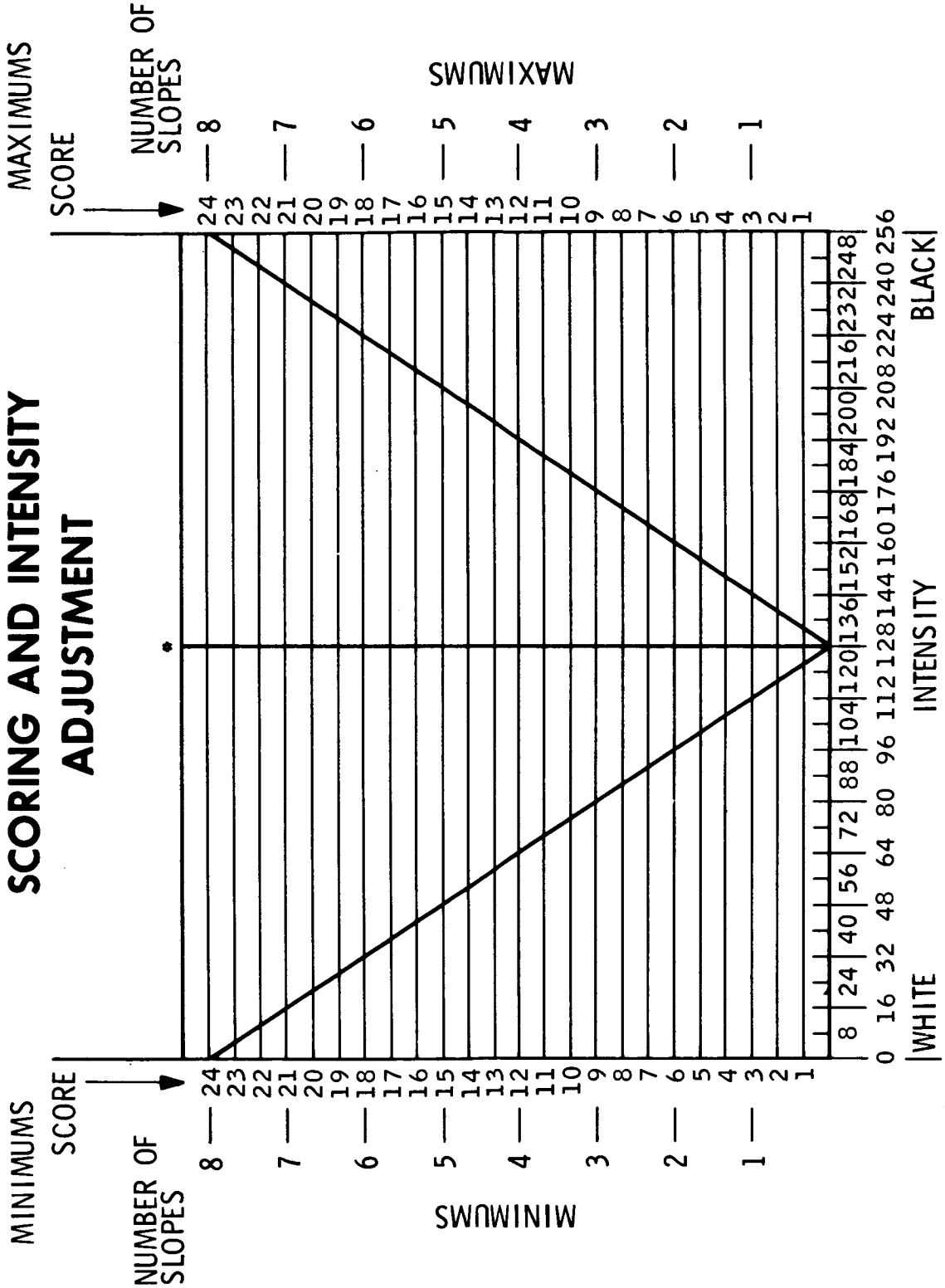

SCORING AND INTENSITY ADJUSTMENT
MINIMUMS
SCORE
NUMBER OF SLOPES
MAXIMUMS
SCORE
NUMBER OF SLOPES
MINIMUMS
MAXIMUMS
0 16 32 48 64 80 96 112 128 144 160 176 192 208 224 240 256
8 24 40 56 72 88 104 120 136 152 168 184 200 216 232 248
WHITE
INTENSITY
BLACK
*MINIMUM EQUALS MAXIMUM

Figure 8-5.

REPLOT AFTER INCREASED AMPLITUDE

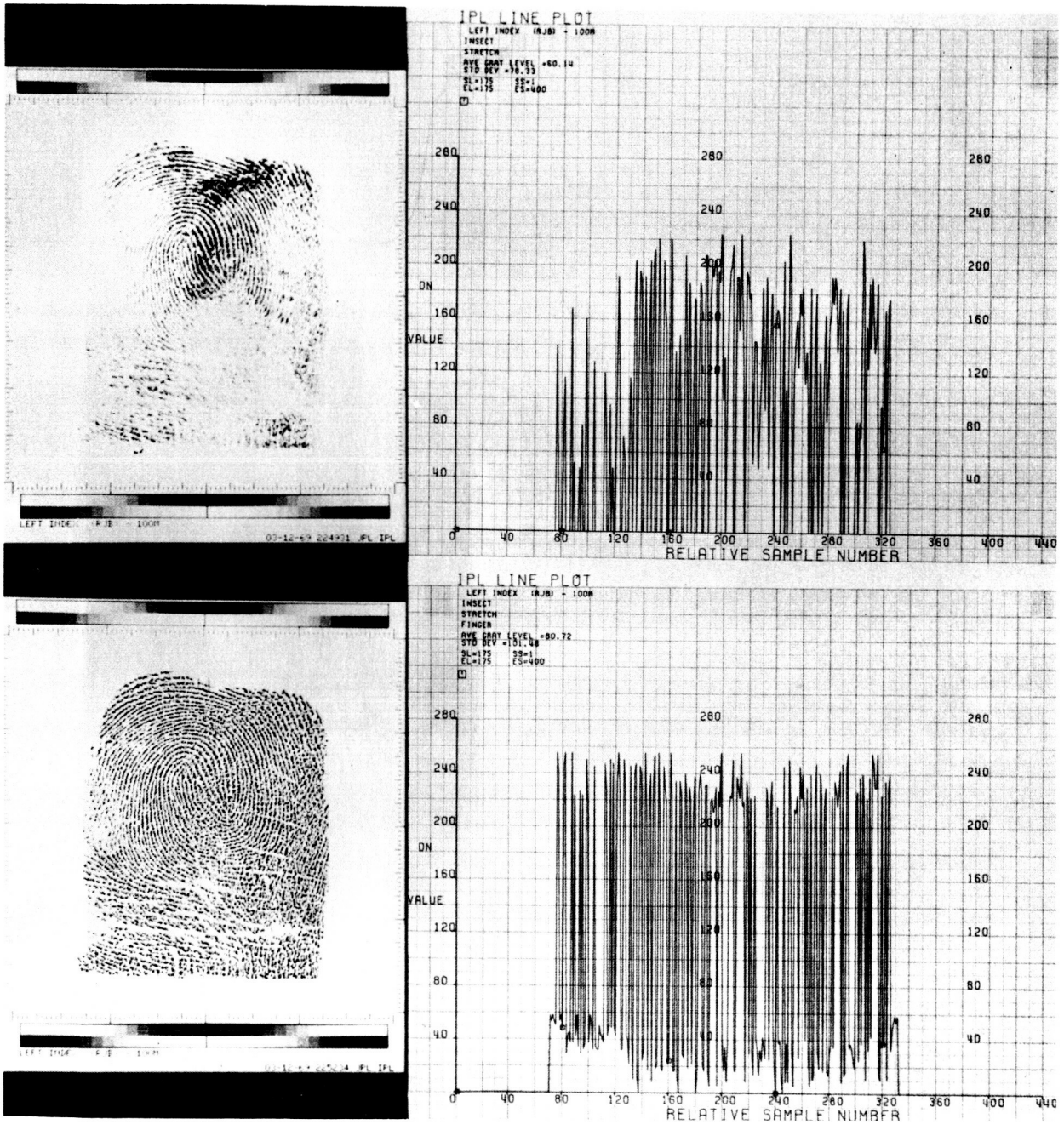


Figure 8-6.

ENHANCED FINGERPRINT ON CLEAR ACETATE

Figure 8-7.

SCAN OF FINGERPRINT FROM STANDARD FINGERPRINT CARD

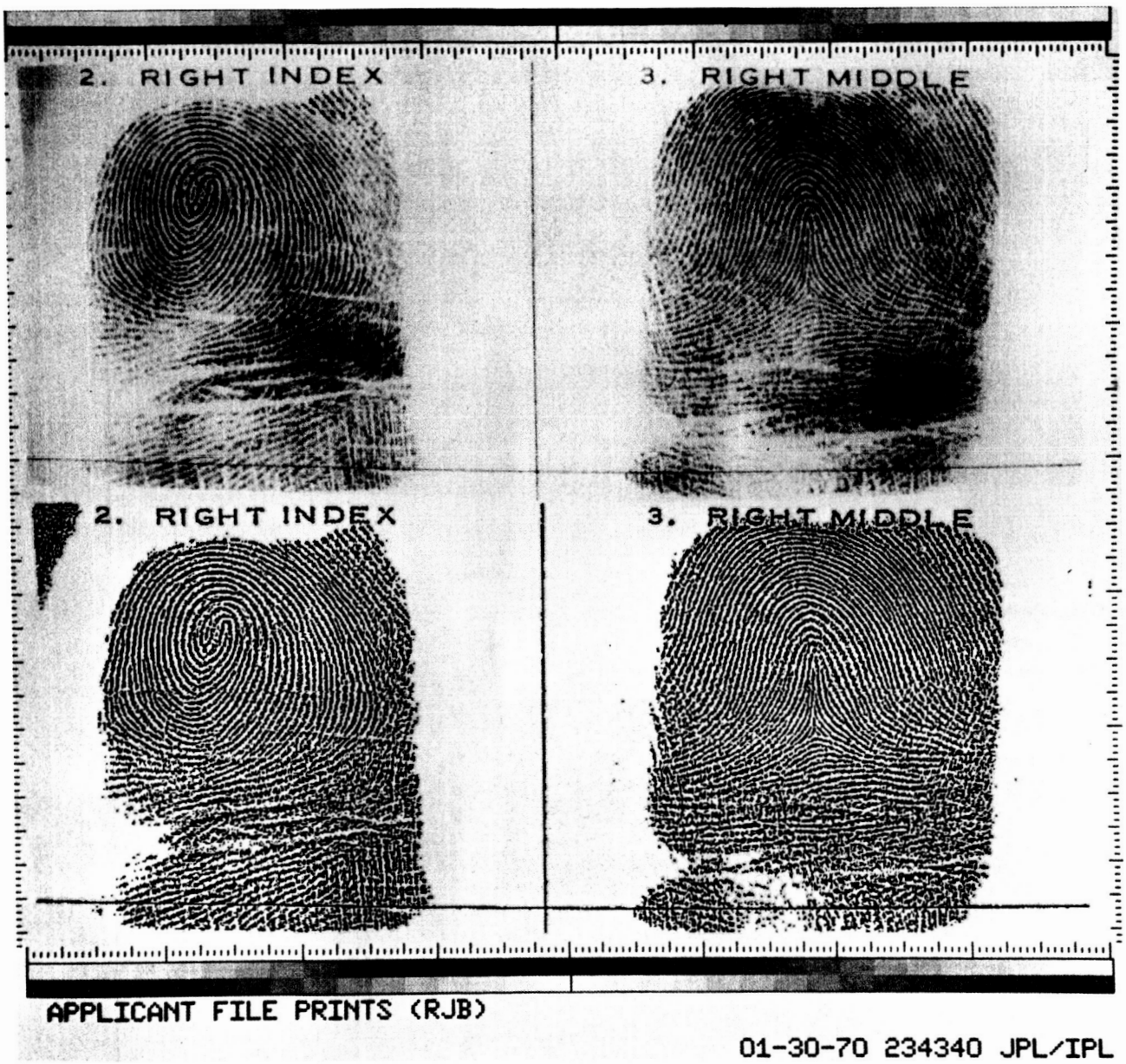


Figure 8-8.

LATENT FINGERPRINTS, ENHANCED

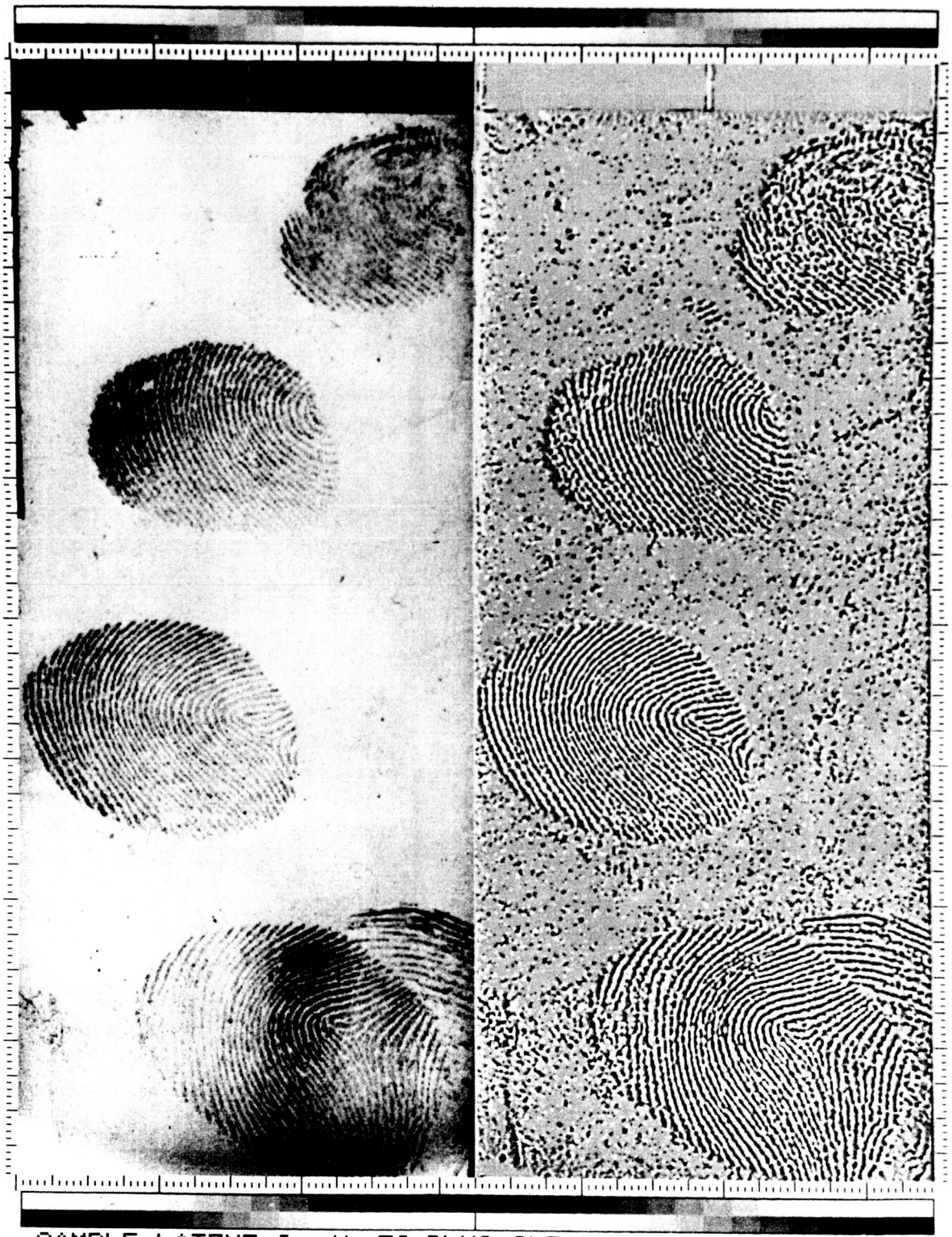


Figure 8-9.

FINGER PORTION OF PALM PRINT, ENHANCED

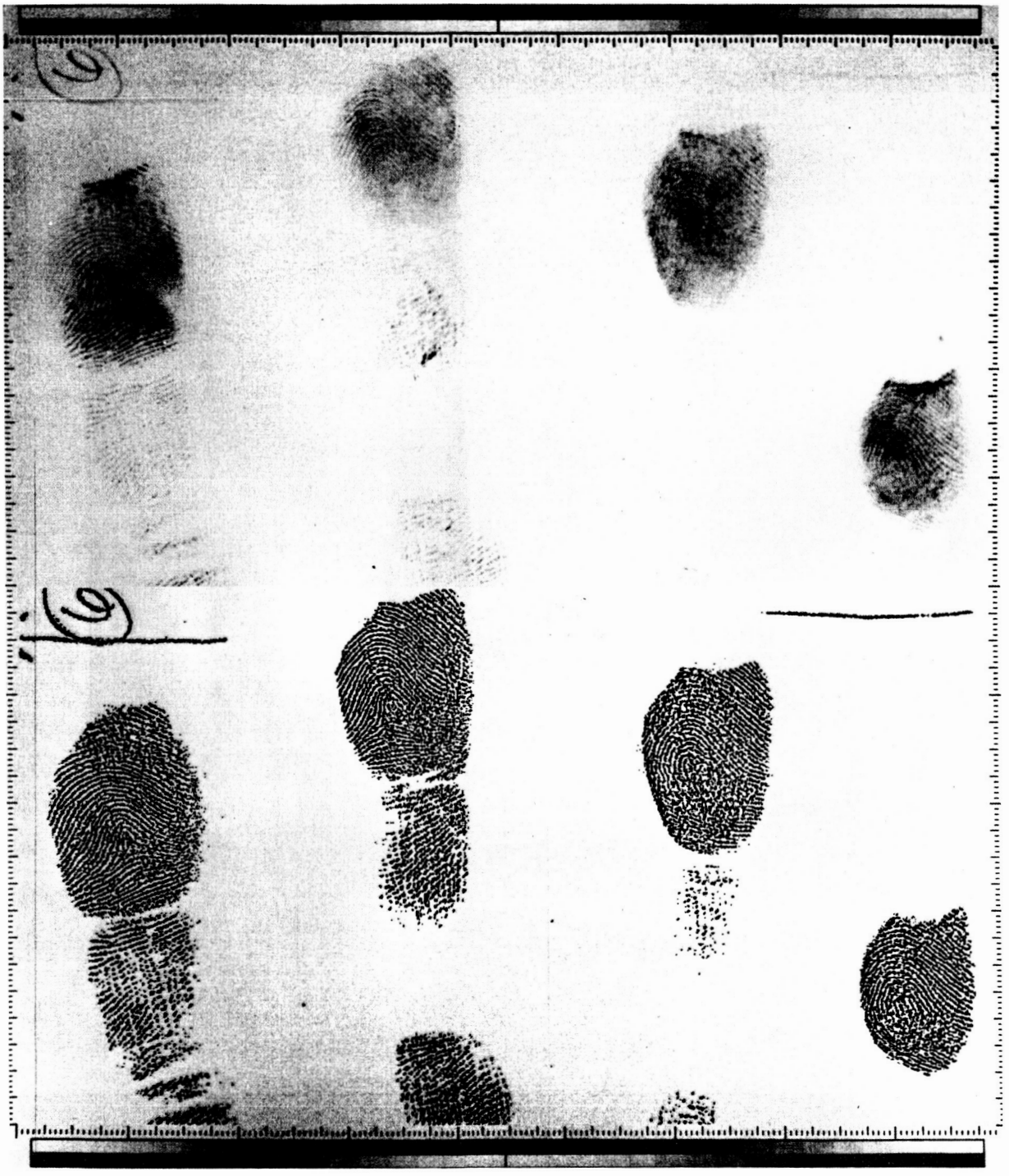


Figure 8-10.

APPENDIX B

Correspondence and Press Clipping

OFFICE OF THE SHERIFF

CONTRA COSTA COUNTY

WALTER F. YOUNG
SHERIFF
P.O. BOX 391
MARTINEZ, CALIFORNIA
94553

D. F. SPENCER

MAY 20 1970

FILE NO.

May 18, 1970

Dr. Dwain F. Spencer
Manager
Space Technology Applications
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91103

Dear Dwain:

I would like to express my appreciation to you and to the Jet Propulsion Laboratory for conducting the Forensic Science Microanalysis Seminar held last week. The five staff members of this laboratory who attended the Seminar all feel that the Seminar will be of extraordinary benefit in applying the techniques of advanced instrumentation to the analysis, identification, and interpretation of physical evidence.

I was very impressed with the abilities of the JPL personnel and the facility with which they were able to convey their knowledge and information to us. I found the availability of the JPL people to discuss various matters with us a very desirable procedure. Rather than a short exposure to the individual at the time of his presentation, the sustained access to the individual throughout the Seminar, during the social hours, lunches and banquet, provided opportunities to discuss factors which did not occur to us during the formal presentation.

I was very pleased and very surprised to learn of certain techniques presented by Bob Rhein which appear to be of direct application to criminalistics work in which the possibility exists of parameters of identification transcending our previously held notions of identification based solely upon chemical constitution. In a number of instances, we were presented with techniques in which the chemical composition of a material could be distinguished from another sample of an identical chemical composition, but with a different history or manner of production.

In addition to the instruction on advanced instrumentation, I found the little procedural hints and aids to sampling techniques presented by Mr. Lawson to be of great interest and benefit. If any consideration is to be given to additional seminars of this type, perhaps some additional information relating to sample handling and UV and IR work could be presented.

The instruction presented on the more sophisticated instruments, such as the mass spectrometer, scanning electron microscope, and electron microprobe was most interesting. Of course, no one would suggest that every laboratory

could manage the fiscal conditions which would be involved in the acquisition of such equipment. The instruction, nevertheless, has made us aware of these very successful techniques and their possible application to problems of physical evidence. From this time forward, this laboratory will not hesitate in attempting to apply these techniques to those occasional cases in which the application of the technique would appear to be conspicuously successful.

The biggest single problem facing the crime laboratory at this point appears to be the burdensome case load of drug and narcotics cases. The AUDRI System, which you are developing, would appear to be addressing this problem and I wish you every success in applying your technology to this very important area.

The staff members of this laboratory who attended this Seminar held a meeting this morning in which we reviewed the material presented. We have already identified several areas in which we believe further consideration will enhance the operation of this laboratory. The Seminar unquestionably has provided the catalyst to enable us to proceed in developing better techniques in a number of diverse areas. Again, I would like to express our gratitude to you and to the Jet Propulsion Laboratory for your willingness to sponsor the Seminar and for the opportunity to be exposed to space technology applications.

A continuation of programs such as this Seminar would be of immeasurable benefit to the field of criminalistics, and I would strongly encourage any efforts which would be made along these lines. Please be assured of our continued cooperation in matters of mutual concern.

Very truly yours,

JOHN I. THORNTON
Chief - Criminalistics Laboratory

JIT/jv

OFFICE OF THE SHERIFF

CONTRA COSTA COUNTY

WALTER F. YOUNG
SHERIFF
P.O. BOX 391
MARTINEZ, CALIFORNIA
94553

May 18, 1970

Mr. Lowell W. Bradford
Director
Laboratory of Criminalistics
Santa Clara County
875 San Pedro Street
San Jose, California 95110

Dear Brad:

I would like to express my appreciation to you for assisting in the arrangements for the Forensic Science Microanalysis Seminar held at the Jet Propulsion Laboratory last week. The five staff members of this laboratory who attended feel that the information we derived from attending the Seminar will be of extraordinary benefit in the analysis, identification and interpretation of physical evidence.

We held a staff meeting this morning and reviewed the Seminar. As a result of a number of items presented, we have already embarked upon several different projects to which we feel laboratory operations will be enhanced. The value of the Seminar to us is practically beyond comprehension, and we would like to express our gratitude to you for your part in sponsoring the Seminar.

Very truly yours,

JOHN I. THORNTON
Chief - Criminalistics Laboratory

JIT/jv

THOMAS C. LYNCH
ATTORNEY GENERAL

CHARLES A. O'BRIEN
CHIEF DEPUTY ATTORNEY GENERAL

STATE OF CALIFORNIA

D. F. SPENCER
O. J. HAWKINS
DEPUTY DIRECTOR
A. L. COFFEY
CHIEF OF BUREAU

MAY 20 1970

FILE NO.

BUREAU OF CRIMINAL IDENTIFICATION AND INVESTIGATION

Department of Justice

3301 C STREET

MAIL ADDRESS
P. O. Box 1659
SACRAMENTO 95809

May 19, 1970

Mr. Dwain Spencer
Manager of STA Division
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, Ca. 91103

Dear Mr. Spencer:

I would like to thank you for the forensic science seminar that was held at your facilities. I think you have performed a great service to the criminal justice system in general and the criminalistics laboratories in particular. Your staff has shown that our limited thinking has kept criminalistics, as a science, about five years behind the times, although we have made strides in our own way. You have opened my eyes to the immense possibilities for applications studies in the field. We have been working on a computer analysis of drugs but our coding has been slow and we are falling further and further behind—something must be done!

I must mention that I was most impressed with Mr. Lawson's demonstration of the thermoluminescence. The phenomenon promises to offer a method to analyze samples of physical evidence which now receive less than complete examination, for example, soil, plastics, wood, glass, hair, etc.. These are the samples that first come to mind. I am sure this is not but a partial list of the relative usefulness of the technique. Not only from a scientific point of view but also from the practical standpoint, this technique offers important information at a reasonable cost.

Once again, thankyou. Please call our laboratory if there is any information or help we may provide.

Sincerely,

Frances M. Evans

FRANCES M. EVANS
Forensic Chemist
Criminalistics Laboratory

FME:fc

THOMAS C. LYNCH
ATTORNEY GENERAL

CHARLES A. O'BRIEN
CHIEF DEPUTY ATTORNEY GENERAL

STATE OF CALIFORNIA

Civil Systems Projects Office
MAY 20 1970

J. HAWKINS
DEPUTY DIRECTOR

A. L. COFFEY
CHIEF OF BUREAU

BUREAU OF CRIMINAL IDENTIFICATION AND INVESTIGATION

Department of Justice

3301 C STREET

MAIL ADDRESS
P. O. Box 1659
SACRAMENTO 95809

May 19, 1970

Mr. Howard H. Haglund
Civil Systems Projects Office
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, Ca. 91103

Dear Mr. Haglund:

Mrs. Frances Evans has briefed us this morning on the forensic science seminar you recently completed. From her enthusiasm and information relayed may I congradulate you on an outstanding program.

Should you contemplate future seminars along the same lines we would be most interested in future dates so we may arrange for as many people as possible to attend.

We are particularly interested in the application of computerized data to the forensic sciences and will shortly have access to a computer on a time/share basis. We plan to use the drug data which was utilized in your AUDRI program.

With our Criminal Information Justice System (CJIS) we would be able to furnish this type of information to all criminalistics laboratories in the State through our telecommunication system.

Should you desire to test some of your instruments using criminalistics laboratories we would be most interested in participating.

If we can assist you in any way, please feel free to call upon us.

Sincerely,

FRED H. WYNBRANDT
Supervising Criminalist
Criminalistics Laboratory

FHW:fc

H. H. HAGLUND
MAY 20 1970

THOMAS C. LYNCH
ATTORNEY GENERAL

CHARLES A. O'BRIEN
CHIEF DEPUTY ATTORNEY GENERAL

STATE OF CALIFORNIA

D. F. SPENCER
DEPUTY DIRECTOR

O. J. HAWKINS
DEPUTY DIRECTOR

A. L. COFFEY
CHIEF OF BUREAU

MAY 27 1970

FILE NO.

BUREAU OF CRIMINAL IDENTIFICATION AND INVESTIGATION

Department of Justice

3301 C STREET

MAIL ADDRESS
P. O. BOX 1659
SACRAMENTO 95809

May 25, 1970

Dwaine F. Spencer, Manager
Space Technology Applications
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91103

Dear Mr. Spencer:

I wish to express my appreciation for the Forensic Sciences Micro-Analysis Seminar which the Jet Propulsion Laboratory presented last week-end. Though I am familiar with most of the instrumentation and its capabilities that were presented at the seminar, one still picks up new bits of knowledge each time that one of these sessions is attended.

I might add that the problems of the various laboratories over the state differ, and I believe Mr. Robert Chamberlain discovered this at the informal workshop which he conducted on Saturday evening.

I will be leaving the employment of the state and assuming the position of Crime Laboratory Supervisor for the state of Illinois on July 1. I would like to inquire if it would be possible for groups from outside the state of California to participate in such a seminar if L.E.A.A. funds were made available.

I would like to be kept advised of any future programs Jet Propulsion Laboratory may offer along these lines. My address as of July 1 will be; 515 East Woodruff Road, Joliet, Illinois, 60432.

There will be no expense claim voucher submitted by me as I continued on state business from the session.

Sincerely,

Theodore R Elzerman

THEODORE R. ELZERMAN
Criminalist

TRE:hlp

JET PROPULSION LABORATORY *California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California 91103*

25 May 1970

Refer to: 511-DFS:ss

Mr. John F. Williams
San Francisco Police Department
Crime Laboratory
San Francisco, California 94103

Dear Mr. Williams:

It was indeed a pleasure for the Jet Propulsion Laboratory **and the** National Aeronautics and Space Administration to host you and other forensic scientists to discuss "The Potential of Advanced Instrumentation Techniques to Forensic Science." The attendance of some 50 individuals exceeded our expectations, and their interest in and attention to the presentations demonstrated the appropriateness of the seminar.

Thank you for finding time in your busy schedule to attend the seminar. It was a pleasure to meet many of you personally, and I hope to meet you all again at a later time.

We at JPL hope that the seminar has provided a means whereby technological capability developed from NASA sponsorship can be transferred to local agencies. It is recognized that this is only a first step in the process; a continuation and amplification of these discussions is certainly necessary to help you solve your many problems. You are cordially invited to initiate additional discussions with any of our staff in areas wherein our capability might assist you. It is desirable to coordinate such activities, so we are requesting that you contact myself (Telephone 213-354-6852) or Mr. Robert Diehl (Telephone 213-354-6811) to schedule these activities.

In order to assess our ability to assist you, we will be contacting you again in three to four months to ascertain what immediate value, if any, your organization has accrued from the seminar. Thank you again for your interest.

Yours very truly,

Dwain F. Spencer, Manager
Space Technology Applications

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Technology of Space Spawns New Crime Detection Methods

Advanced Techniques, Developed for Enhancing Pictures From Mars, May Be Applied to Fingerprint Identification

BY MARVIN MILES
Times Aerospace Writer

No one at Caltech's Jet Propulsion Laboratory will be surprised if some future murder is solved by processes used to enhance pictures of Mars or study Martian soil millions of miles distant.

By sharpening a hopelessly smudged fingerprint with computer techniques or linking two infinitesimal pieces of dirt to a common source with automated laboratory techniques designed for space use, a suspect could be tied tightly to a crime—or exonerated.

At JPL, the solution would be credited to Space Age technology turned to the earthly advantage of the criminalist, the man who investigates crime scientifically as opposed to the criminologist who studies its causes.

Criminalists—or forensic scientists—from crime laboratories throughout California met with experts at JPL over the weekend to study the law enforcement potential of cosmic exploration.

Called a microanalysis seminar, the unique session was sponsored by the National Aeronautics and Space Administration and JPL's Space Technology Applications Office, in cooperation with the California Council on Criminal justice.

Its aim: to examine how Space Age techniques might be employed to improve and accelerate scientific investigation procedures, particularly the analysis and evaluation of physical evidence.

"Other than the overburdened FBI crime laboratory in Washington, there are few centers equipped for thorough study of physical evidence," explained Dwain F. Spencer, manager of JPL's Space Technology Applications Office.

"In many cases there is no effort to use such evidence simply because there are no methods and no equipment available to take advantage of it.

"At JPL we are working on the application of several techniques that appear very promising and others that could have great potential, although we have no solutions at this point.

"In this pilot meeting—which may be followed by others across the country—we are attempting only to expose the criminalists to possibilities and potential approaches."

Funds Now Available

The JPL engineer noted that the Omnibus Crime Act of 1968, which set up the Law Enforcement Assistance Administration, provided $250 million for research and development in police work this year, which could be increased to $480 million or more in fiscal 1971.

"This brings great encouragement to crime labs which hope to modernize their equipment and to the smaller centers which could contract for scientific work as needed.

"In the past there was no hope because 95% of the available money went into operations."

Of the seven or eight techniques discussed and demonstrated at the Jet Lab seminar, several deal with the identification of narcotics—or lack of them—in the case of suspected users.

Generalities in classifying narcotics in a suspected crime are no longer permissible under new laws that require that drugs must be identified specifically, both those found on a person and those he has taken into his system.

This makes scientific investigation more difficult, demanding particularly definitive analysis that could clear a suspect as well as establish his guilt, Spencer emphasized.

The four JPL systems having the most potential include:

—Fingerprint image enhancement by computer methods, a technique based on JPL's development of a digital computer system for improving the contrast and resolution of pictures received from cameras aboard Ranger, Surveyor and Mariner spacecraft.

X-Ray Use

These computer methods also have been successfully applied by JPL to the image enhancement of medical X-rays and biological micro-photographs and can bring out fingerprints heretofore regarded as impossible.

—The scanning electron microscope is used in space work to evaluate tiny electronic spacecraft circuits and determine their quality. The microscope can look into the fine structure of physical evidence and identify the smallest pieces through a variety of detail.

Types of samples studied to date with this searching instrument include blood cells, algae, hair fibers, insects, spores, botanical material, metal, paper, glass, paint and organic polymers, together with electronic components.

—Thermoanalytical methods that include the heating of various materials for comparative analysis through weight loss established by supersensitive electronic balance mechanisms.

This system, designed to prove or disprove the common origin of two samples of material was initially developed to study the outgassing or loss of normal internal gasses from materials in the vacuum of space.

A thermoanalytical system, it is calculated, could be made available to crime laboratories for about $2,000.

Automated drug identification is perhaps JPL's best space technology application — at least the most advanced of current developments.

This is a fully automatic system that takes a sample of blood or urine, puts it through a wet chemical process to precipate a particular material, then feeds it to a gas chromatograph to separate it into fractions that are in turn analyzed for specific drug components by an infrared spectrometer.

The entire process is controlled by a minicomputer that analyzes the result and compares it with its own bank of data on 100 drugs that are most common (98%) in police work, then prints out a specific analysis.

Estimated cost of an operational automated drug identification system is about $50,000, but it could handle 12 cases a day with a single operator, whereas four technologists are now required to check eight cases a day.